The Coordination Chemistry of Phosphoryl Compounds Containing
the $-N(CH_3)_2$ Group, Part XI¹

Complexes of Bismethyl-imido-triphosphoric-acid-pentakisdimethyl-amide (TRIPA), a New Tridentate Ligand

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TRIPA, coordination chemistry, phosphoryl compounds

A number of new complexes containing TRIPA, chemical formula $[(CH_3)_2N]_2P(O)N(CH_3)P(O)[N(CH_3)_2]N(CH_3)P(O)[N(CH_3)_2]_2$, is reported. The compounds have the general formula $M(TRIPA)_n(\text{anion})_p$, where $M = \text{Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd}$ ($p=2$) and Al, Fe ($p=3$), $n=1, 2$ and anion stands for BF_4^- , $[\text{B}(\text{C}_6\text{H}_5)_4]^-$, NO_3^- and Cl^- . They are characterized and identified by chemical analysis and physical measurements.

It is shown that the *bis*-compounds contain octahedrally solvated metal ions, the ligand acting as a tridentate phosphoryl donor. Electron paramagnetic resonance measurements show some distortion of the octahedrons. The *mono*-compounds with the nitrate anion probably possess a five-coordinated structure whereas the chloride complexes are probably dimeric.

The occurrence of more than one geometric isomer for the group $[M(TRIPA)_2]^{p+}$ is discussed. It is concluded that the *s-facial* and *u-facial* isomers may occur; a possible connection with the size of the metal ions is indicated. The *mer* form is rejected because of steric requirements.

Tridentate ligands of the form $A-A-A$, where A is the coordinating atom, are relatively rare in coordination chemistry. With nitrogen as the donor atom A , an example is diethylenetriamine(dien). The three possible geometric isomers of the complexes $[\text{Co}(\text{dien})_2]\text{X}_3$ ($\text{X} = \text{Cr, Br, I}$) were recently reported². The optical isomers of the *mer* and *u-facial* forms were resolved by means of column chromatography².

In a recent set of papers we studied the coordination chemistry of hexamethylphosphoramide (HMPA) and nonamethylimidodiphosphoramide (NIPA)^{1, 3-10}. Since NIPA (which can be looked upon as consisting of two "fused" HMPA molecules) showed an unusual tendency to form solvated metal ions, it seemed interesting to study the coordination chemistry, and especially the solvating properties, of TRIPA (which can be looked upon as consisting of three "fused" HMPA molecules).

The present paper therefore describes the preparation and identification of a number of TRIPA complexes. As far as we know, no solvates of a neutral tridentate oxygen donor have been reported in the literature.

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Experimental part

Starting materials

Most metal salts were commercially available (as hydrates) or were prepared by standard procedures¹¹. The preparation of TRIPA will shortly be published¹².

Preparation of the complexes

The hydrated metal salt was dissolved in acetone and trimethyl orthoformate was added (for dehydration¹³). The ligand was added in a solution in A.R. grade acetone. Upon standing, crystals of the complexes appeared, in a few cases only after concentration of the solution or after addition of some dry diethyl ether. The crystals were filtered, washed with dry diethyl ether and finally dried *in vacuo* at room temperature.

Changing the solvent to methanol or methyl cyanide, or changing the metal salt to ligand ratio (from 1:1 to 1:2, or *vice versa*) did not influence the results.

The tetraphenylborate complex was prepared by adding a solution of $\text{NaB}(\text{C}_6\text{H}_5)_4$ in A.R. grade acetone to a solution of $\text{Co}(\text{TRIPA})_2(\text{BF}_4)_2$ in A.R. grade acetone (in the ratio 2:1).

Most of the complexes are hygroscopic and must be handled in a dried glove-box.

Measurements

Semi-micro metal analyses were carried out by complexometric titrations. Infrared spectra were recorded on an Unicam SP 1200 ($4000-400\text{ cm}^{-1}$) and a Hi-

tachi EPI-L ($700-200\text{ cm}^{-1}$) spectrophotometer, using nujol mulls sandwiched between potassium bromide and polythene windows. Ligand-field spectra of the solid compounds were obtained with a Beckman DK-2A ratio recording spectrophotometer, using magnesium oxide as a reference, in the $325-2500\text{ nm}$ region. X-ray powder diagrams were obtained with a Guinier type powder camera using $\text{Cu-K}\alpha$ radiation. The samples were mounted with vaseline and protected from atmospheric vapour by adhesive tape. Conductivity measurements were carried out with a Philips cell, type GM 4221, and a Philips conductivity bridge, type 4249. Electron paramagnetic resonance measurements were performed on a Varian E-3 apparatus using X-band frequencies. The spectra of the powdered solid compounds were run as the first derivative. Galvanoxyl was used as a reference compound.

Results

General

In Table I the coordination compounds concerning the present work are listed together with their analytical results, colours and melting points. Further in this Table the X-ray types for the several compounds are indicated by the symbols A – C. The division into these groups was made according to the X-ray powder diagrams of the compounds, which were very similar in $d(\text{\AA})$ values and intensities for members of the same group. The differences in line

patterns for the compounds marked with an accent and the unmarked ones are only very small. These similarities in X-ray powder patterns strongly suggest isomorphism between the several compounds of the same group.

In Table II the conductivities of some complexes in methyl cyanide are listed. The data for the *bis*-compounds correspond to those for 1:2 electrolytes and the data for the *mono*-complexes correspond to those for 1:1 electrolytes^{14, 15}.

Table II. Conductivities of 10^{-3} M solutions in methyl cyanide at room temperature.

Compound	Λ_{M} $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$
$\text{Zn}(\text{TRIPA})_2(\text{BF}_4)_2$	325
$\text{Cd}(\text{TRIPA})_2(\text{BF}_4)_2$	260
$\text{Mg}(\text{TRIPA})_2(\text{NO}_3)_2$	315
$\text{Mn}(\text{TRIPA})(\text{NO}_3)_2$	160
$\text{Cu}(\text{TRIPA})(\text{NO}_3)_2$	115
$\text{Zn}(\text{TRIPA})(\text{NO}_3)_2$	134
$\text{Cd}(\text{TRIPA})(\text{NO}_3)_2$	100

Infrared spectra

The phosphoryl stretching and bending vibrations for the free ligand are found at 1226 and 502 cm^{-1} , respectively. In the complexes, these frequencies are shifted to lower and higher energy, respectively, in-

Table I. Complexes of TRIPA; analyses, colours, melting points and X-ray types.

Compound	Metal [%] found	calcd	Colour	Melting point [°C]	X-ray type
$\text{Ca}(\text{TRIPA})_2(\text{BF}_4)_2$	3.89	3.81	white	198–200	A
$\text{Mn}(\text{TRIPA})_2(\text{BF}_4)_2$	4.99	5.15	white	161–163	A
$\text{Fe}(\text{TRIPA})_2(\text{BF}_4)_2$	5.33	5.22	cream	136–138	B
$\text{Co}(\text{TRIPA})_2(\text{BF}_4)_2$	5.45	5.50	pink	216–218	B
$\text{Ni}(\text{TRIPA})_2(\text{BF}_4)_2$	5.55	5.48	yellow-green	194–195	B
$\text{Cu}(\text{TRIPA})_2(\text{BF}_4)_2$	6.07	5.91	blue-green	119–120	A'
$\text{Zn}(\text{TRIPA})_2(\text{BF}_4)_2$	6.00	6.07	white	200–202	B
$\text{Cd}(\text{TRIPA})_2(\text{BF}_4)_2$	10.1	9.99	white	207 dec.	A
$\text{Co}(\text{TRIPA})_2[\text{B}(\text{C}_6\text{H}_5)_4]_2$	3.77	3.86	pink	199–201	—
$\text{Mg}(\text{TRIPA})_2(\text{NO}_3)_2$	2.51	2.46	white	93–95	—
$\text{Ca}(\text{TRIPA})(\text{NO}_3)_2$	6.78	6.87	white	133–135	—
$\text{Mn}(\text{TRIPA})(\text{NO}_3)_2$	8.95	9.18	white	174–176	—
$\text{Co}(\text{TRIPA})_2(\text{NO}_3)_2$	5.85	5.77	light violet	120–122	B
$\text{Ni}(\text{TRIPA})_2(\text{NO}_3)_2$	5.77	5.74	yellow-green	169–170	B
$\text{Cu}(\text{TRIPA})(\text{NO}_3)_2$	10.4	10.5	blue	170–171	—
$\text{Zn}(\text{TRIPA})(\text{NO}_3)_2$	10.7	10.7	white	99–102	—
$\text{Cd}(\text{TRIPA})(\text{NO}_3)_2$	16.9	17.1	white	137–139	—
$\text{Al}(\text{TRIPA})_2(\text{NO}_3)_3$	2.63	2.57	white	217 dec.	—
$\text{Fe}(\text{TRIPA})_2(\text{NO}_3)_3$	5.25	5.17	yellow	60–65	—
$\text{Co}(\text{TRIPA})\text{Cl}_2$	10.8	10.7	blue	182–184	C
$\text{Ni}(\text{TRIPA})\text{Cl}_2$	10.6	10.7	blue-green	196–198	C'

— denotes a type different from any other.

dicating that coordination has occurred *via* the oxygen atoms of the ligand^{3, 4, 10, 16}.

It is well known that infrared spectra of BF_4^- and NO_3^- ions can provide evidence about coordination to metal ions, since lowering of the symmetry dramatically influences the number of infrared absorptions^{10, 16}. As regards the BF_4^- complexes of TRIPA, no signs of symmetry lowering were found; all compounds showed a strong band at $\sim 1050 \text{ cm}^{-1}$, due to the ν_3 mode of the BF_4^- ion¹⁶.

The infrared absorptions of the nitrate ions that are not masked by ligand absorptions, are listed in Table III. As can be seen from this Table, the *bis*-compounds showed only one absorption for the ν_3 mode and a very weak absorption for the ν_1 mode. This indicates uncoordinated nitrate ions in these complexes^{10, 16}. The spectra of the *mono*-compounds,

however, are in agreement with coordinated nitrate ions^{10, 16}.

The chloride complexes showed strong absorptions at 285 (Co^{2+}) and 290 (Ni^{2+}) cm^{-1} . These bands can be attributed to the ν_3 mode of the $(\text{MCl}_4)^{2-}$ anions (see also below)¹⁶.

Finally, it is remarked that the trivalent nitrate complexes showed strong absorptions at 570 and 650 cm^{-1} (Al^{3+}), and 550 cm^{-1} (Fe^{3+}), which could not be attributed to ligand or anion modes. In view of the results found for the corresponding NIPA complexes, we assign these bands to metal-ligand stretching vibrations^{5-7, 10}. In agreement with earlier results, no signs of such bands were found in the case of the bivalent complexes^{4-7, 10}.

Ligand-field spectra

For evidence about the coordination around the metal ions, and the ligand-field strength of TRIPA, reflectance spectra of the solid compounds of Fe(II), Co(II), Ni(II) and Cu(II) were taken. In Table IV the band maxima, assignments and calculated values of the ligand-field parameters Dq , B , Dq/B and β are given. Assignments and calculations are in accordance with refs. 17-23.

The absorption bands for the compounds $\text{M}(\text{TRIPA})_2(\text{anion})_2$, where $\text{M} = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}$, and anion stands for BF_4^- , NO_3^- and $[\text{B}(\text{C}_6\text{H}_5)_4]^-$, correspond with an octahedral environment of the metal ions¹⁷⁻¹⁹. The band maxima

Table III. Infrared absorptions of the nitrate groups in TRIPA complexes (cm^{-1}).

Compound	$\nu_2(\text{NO}_3^-)$	$\nu_1(\text{NO}_3^-)$	$\nu_3(\text{NO}_3^-)$
$\text{Mg}(\text{TRIPA})_2(\text{NO}_3)_2$	830 w	1038 vw	1345 s
$\text{Ca}(\text{TRIPA})(\text{NO}_3)_2$	826 m	1037 m	1325 s, 1415 s
$\text{Mn}(\text{TRIPA})(\text{NO}_3)_2$	822 m	1033 m	1310 s, 1450 s
$\text{Co}(\text{TRIPA})_2(\text{NO}_3)_2$	830 w	1038 vw	1340 s
$\text{Ni}(\text{TRIPA})_2(\text{NO}_3)_2$	830 w	1038 vw	1345 s
$\text{Cu}(\text{TRIPA})(\text{NO}_3)_2$	813 m	1025 m	1325 s, 1460 s
$\text{Zn}(\text{TRIPA})(\text{NO}_3)_2$	813 m	1026 m	1300 s, 1460 s
$\text{Cd}(\text{TRIPA})(\text{NO}_3)_2$	824 m, 828 m	1036 m, 1040 m	1340 s, 1400 m, 1450 s
$\text{Al}(\text{TRIPA})_2(\text{NO}_3)_3$	830 w	1038 vw	1340 s
$\text{Fe}(\text{TRIPA})_2(\text{NO}_3)_3$	830 w	1038 vw	1345 s

Abbreviations: s = strong, m = medium, w = weak, v = very.

Table IV. Ligand-field spectral data of some TRIPA complexes; band maxima are in kK, Dq and B in cm^{-1} , Dq/B and β are real numbers.

Compound	Band maxima and assignments				Dq^*	B^*	$Dq/B^* \beta^*, \dagger$
	${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$	${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$	${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$			
$\text{Ni}(\text{TRIPA})_2(\text{BF}_4)_2$	7.69	13.1	14.6 sh	23.5	769	902	0.85
$\text{Ni}(\text{TRIPA})_2(\text{NO}_3)_2$	7.72	13.1	14.5 sh	23.4	772	892	0.86
$\text{Ni}(\text{TRIPA})\text{Cl}_2$	=	=	=	23.5	—	—	—
		${}^4\text{T}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$	${}^4\text{A}_{2g}, {}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$				
$\text{Co}(\text{TRIPA})_2(\text{BF}_4)_2$		7.19	14.2,	19.0	778	858	0.91
$\text{Co}(\text{TRIPA})_2(\text{NO}_3)_2$		7.20	14.2,	18.9	780	850	0.92
$\text{Co}(\text{TRIPA})_2[\text{B}(\text{C}_6\text{H}_5)_4]_2$		7.19	14.1,	18.9	778	851	0.91
$\text{Co}(\text{TRIPA})\text{Cl}_2$		=	=,	18.9	—	—	—
		${}^5\text{E}_g \leftarrow {}^5\text{T}_{2g}$					
$\text{Fe}(\text{TRIPA})_2(\text{BF}_4)_2$		9.72			972	—	—
$\text{Cu}(\text{TRIPA})_2(\text{BF}_4)_2$		11.5			—	—	—
$\text{Cu}(\text{TRIPA})(\text{NO}_3)_2$		11.8			—	—	—

Abbreviations: sh = shoulder. $\dagger \beta = B/B_0$; $B_0 = 971 \text{ cm}^{-1}$ (Co^{2+}), 1030 cm^{-1} (Ni^{2+})²³. * Accuracies: Dq , B and $\beta \pm 2\%$, $Dq/B \pm 3\%$. † Masked by absorptions of the $(\text{MCl}_4)^{2-}$ ions (see text).

for the Cu(II) complexes correspond with distorted octahedrally coordinated Cu^{2+} ions²².

Besides absorptions due to the moiety $[\text{M}(\text{TRIPA})_2]^{2+}$, strong absorptions at 5.40 and 14.8 kK (Co^{2+}), and 7.27 and 14.8 kK (Ni^{2+}) were found in the spectra of the chloride complexes. These band maxima correspond to those reported for the anions $(\text{CoCl}_4)^{2-}$ and $(\text{NiCl}_4)^{2-}$, respectively^{20, 21}.

Discussion

From the results described above, it can be concluded that all *bis*-complexes contain solvated metal ions. This is based on the following observations:

- Infrared spectroscopy indicated the presence of uncoordinated anions and only coordinated phosphoryl groups.
- Conductivity measurements indicated the presence of 1:2 electrolytes (at least in methyl cyanide solutions).
- Ligand-field spectroscopy indicated an identical first coordination sphere for all *bis*-compounds of a certain metal ion.
- X-ray powder diagrams indicated isomorphism between complexes with different anions; this strongly resembles the behaviour of the NIPA solvates^{5, 10}.

It follows thus that we can assign a solvate structure to all *bis*-complexes, *i. e.* $[\text{M}(\text{TRIPA})_2]^{n+}(\text{anion}^-)_n$.

As regards the ligand-field parameters of TRIPA, it is remarked that TRIPA possesses a higher Dq value and a lower B value than NIPA⁴. The metal-oxygen distances in the TRIPA solvates may be smaller than in the corresponding NIPA solvates.

The most typical aspect of a *bis*-tridentate solvate is that it can exist in three different geometric forms: the *mer*, *s-facial* and *u-facial* isomers². Generally speaking, they can only be resolved by structure determinations and by special optical measurements (the *s-facial* isomer contains a center of symmetry, the *u-facial* and *mer* forms not)². However, some remarks concerning the particular isomers that may be present, can be made:

Because the complexes were obtained as crystals and because different preparations yielded compounds with identical X-ray powder patterns, it seems unlikely that isomer mixtures are present.

When one builds models for the various isomers, it can be seen that the *mer* form is very unfavourable because of steric reasons. We may therefore exclude the possibility that this isomer occurs among our complexes.

As regards the X-ray types of the tetrafluoroborate solvates, it is interesting to note that the larger metal ions possess a different X-ray type (type A) than the smaller metal ions (type B)²⁴. It might be possible that this is connected with the presence of *s-facial* and *u-facial* isomers (compare also the results obtained for NIPA⁴⁻¹⁰).

An electron paramagnetic resonance spectrum of pure $\text{Mn}(\text{TRIPA})_2(\text{BF}_4)_2$ consisted of a single line near $g_{\text{eff}} = 2$; this is common for Mn(II) compounds near $g_{\text{eff}} = 2$; this is common for Mn(II) compounds of the Zn(II) and Cd(II) dopes showed considerable hyperfine-structure; the magnitude of the hyperfine splitting constant (A) was found to be 95 Gs. This A value is in the usual range for oxygen donor ligands coordinated to Mn(II)^{25, 26}.

Undiluted $\text{Cu}(\text{TRIPA})_2(\text{BF}_4)_2$ yielded an asymmetric EPR spectrum with $g_{\parallel} = 2.39$ and $g_{\perp} = 2.08$, no hyperfine structure upon $g_{\parallel}$ was resolved. When Cu(II) was doped in the lattices of $\text{Zn}(\text{TRIPA})_2(\text{BF}_4)_2$ and $\text{Cd}(\text{TRIPA})_2(\text{BF}_4)_2$, the parameters were, for Zn: $g_{\parallel} = 2.43$ and $g_{\perp} = 2.07$, for Cd: $g_{\parallel} = 2.46$ and $g_{\perp} = 2.09$ ($A_{\parallel} = 95$ Gs). The magnitudes of the several parameters agree with oxygen-coordinated ligands to Cu(II)²⁵. For all three cases, the spectra correspond with distorted species $[\text{Cu}(\text{TRIPA})_2]^{2+}$ ²².

However, the EPR spectrum of the manganese(II) doped Cd(II) compound showed more distortion than that of the manganese(II) doped Zn(II) compound. Since the models that we built showed more irregularity in the case of the *u-facial* isomer, we assign this form to the Cd compound (and therefore to all complexes of X-ray type A) and the *s-facial* form to the Zn compound (and thus to all complexes of X-ray type B). It is however emphasized that this assignment is only tentative. A definite assignment can only be reached by structure determinations in combination with special optical measurements; studies on these subjects are currently in progress.

As regards the structures of the chloride complexes, all measurements indicated the presence of the species $(\text{MCl}_4)^{2-}$. The dimeric-ionic structure $[\text{M}(\text{TRIPA})_2]^{2+}(\text{MCl}_4)^{2-}$ can therefore be assigned to these complexes. With NIPA, we found a cor-

responding structure (*i. e.* $[M(NIPA)_3]^{2+}(MCl_4)^{2-}$) for the Ni(II) compound⁴, but with $CoCl_2$ a tetrahedral adduct, $Co(NIPA)Cl_2$, was obtained⁴. It can therefore be said that TRIPA has more solvating "power" than NIPA.

The nitrate complexes of formula $M(TRIPA)(NO_3)_2$ (the *mono*-compounds) present some interesting problems. With the exception of the Cd(II) complex, the infrared spectra indicated the presence of equivalent coordinated nitrate groups. However, the conductivity measurements suggested the presence of 1:1 electrolytes in methyl cyanide solution. It follows then that methyl cyanide solvation must have occurred (otherwise the measurements would contradict each other). We assume therefore that the solid compounds are non-electrolytes (see above). Because of the fact that the nitrate groups are equivalent and no uncoordinated phosphoryl groups are present (see above), the only possibility is a five-coordinated structure of the type $[M(TRIPA)(ONO_2)_2]$, with monodentate coordinated nitrate groups.

For the sake of completeness, it is remarked that a dimeric-ionic structure of the type $[M(TRIPA)_2]^{2+}[M(NO_3)_4]^{2-}$ is ruled out by the infrared spectral measurements and, in the case of Cu(II), by its ligand-field spectrum²⁷.

As regards the five-coordinated structure, models showed that a basically square pyramidal structure is more likely than a trigonal bipyramidal one (because of steric reasons); this is as expected for oxygen donor ligands²⁸. Various geometric isomers are again possible.

Finally, the compound $Cd(TRIPA)(NO_3)_2$ is left. Its infrared spectrum clearly indicated the presence of non-equivalent nitrate groups. Since infrared spectroscopy cannot distinguish between monodentate and bidentate coordinated nitrate ions²⁹ (and, in this case, one of the nitrate groups might even be ionic), the following structures are possible: octahedral $[M(TRIPA)(ONO_2)(O_2NO)]$, five-coordinated $[M(TRIPA)(O_2NO)]^+(NO_3)^-$ and tetrahedral $[M(TRIPA)(ONO_2)]^+(NO_3)^-$. Because of the size of Cd(II), the octahedral structure seems the most likely but a definite assignment cannot be made.

Conclusions

From the results discussed above, the following conclusions can be drawn:

1. The ligand TRIPA is a strongly coordinating agent for many metal ions, yielding solvated metal ions in many cases.
2. In all complexes investigated, TRIPA acts as a tridentate phosphoryl donor.
3. The ligand occurs somewhat above NIPA in the spectrochemical and nephelauxetic series.
4. Depending on the size of the metal ion, both *s-facial* and *u-facial* isomers seem to occur among the tetrafluoroborate solvates.

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Halogenierungs- und Oxidationsreaktionen an Metallchelateverbindungen

Halogenation- and Oxidation-reactions on Metal-chelate Compounds

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Halogenation, Metal Compounds of Acetylacetone, Salicylaldehyde, Salicylicacidmethylester

Reactions of acetylacetonate-, salicylaldehyde- and methylsalicylate-metal compounds with oxygen, bromine and sulfurylchloride were investigated. It was found, that these reactions yield to a variety of products depending on the used central metal ion.

Abkürzungen: Acac = acetylacetonato, Sal = salicylaldehydato, Salm = methyl-salicylato, Py = Pyridin, Pip = Piperidin, Morph = Morpholin.

In Chelatmetallkomplexen kann die Wechselwirkung des Zentralmetallions mit den Chelatliganden durch spektroskopische Methoden, wie beispielsweise KMR- und IR-Spektroskopie, sehr schön nachgewiesen werden. Es schien nun von Interesse zu untersuchen, ob solche spektroskopisch festgestellten Metall-Ligand-Wechselwirkungen Folgerungen für die präparative Chemie an diesen Verbindungen ermöglichen¹.

Es wurden Komplexe des Acetylacetons (Pentandion-2.4), Salicylaldehyds und Salicylsäuremethylesters verschiedenen Halogenierungs- und Oxidationsreaktionen unterworfen und die Reaktionsbedingungen jeweils optimiert. Als Zentralmetallionen wurden sowohl dia- wie auch paramagnetische Metallionen eingesetzt, als zusätzliche Liganden in der Axialstellung der untersuchten pseudo-oktaedrischen Bis-(chelate)-metall(II)-Komplexe wurden Pyridin, Piperidin, Morpholin und Wasser verwendet.

Umsetzungen mit Sulfurylchlorid

Im folgenden sei eine Vorschrift unter optimalen Reaktionsbedingungen, vertretend für alle Umsetzungen mit Sulfurylchlorid, angegeben.

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Zu 0,05 Mol Bis(acetylacetonato)-bis(piperidin)kobalt(II), suspendiert in 75 ml Benzol (Wassergehalt des Benzols 0,06%) wurde innerhalb von 20 Min. unter schnellem Rühren und Kühlen (Eis/Kochsalz) 0,1 Mol Sulfurylchlorid zugetropft. Die entstehende Salzsäure wurde durch die berechnete, bereits vor dem Reaktionsbeginn zugefügte Menge NaHCO₃ neutralisiert. Anschließend wurde das Benzol an der Wasserstrahlpumpe abgezogen und der Rückstand (zu Tränen reizend, ölig) ausgeäthert. Nach dem Trocknen und Abziehen des Äthers bleibt durch Acetylaceton (Pentandion-2.4) und 3-Chlor-pentandion-2.4 stark verunreinigtes 3.3-Dichlor-pentandion-2.4 zurück. Das gleiche Ergebnis wurde erhalten, wenn die Reaktion unter N₂ als Schutzgas oder bei Gegenwart eines Radikalinhibitors (Hydrochinon) durchgeführt wird.

Im Gegensatz zu der Umsetzung des freien Acetylacetons mit der äquivalenten Menge Sulfurylchlorid, die nur zur Monochlorierung des Acetylacetons führt^{2,3}, wird also bei Einsatz des Acetylacetonato-Komplexes das freie dichlorierte Produkt erhalten, während das sicherlich auch gebildete 3-Monochlor-pentandion-2.4 komplex gebunden bleibt.

An Reaktionsbedingungen wurden variiert: die Zutropfzeit des SO₂Cl₂ (zwischen 10 und 240 Min.), die Reaktionstemperatur (sie darf 40 °C nicht überschreiten), die Lösungsmittelmenge (zwischen 50 und 500 ml für 0,05 Mol Komplex), das Neutralisationsmittel (es wurde Morpholin, K₂CO₃ und NaHCO₃ verwendet), der Wassergehalt des Lösungsmittels (zwischen 0,00 und 0,07%) und, wie bereits angeführt, der Axialligand.

Unter den oben genannten Reaktionsbedingungen wurden im Reaktionsprodukt etwa 80% 3.3-Dichlor-pentandion-2.4 gefunden. Wird der Wassergehalt des Lösungsmittels Benzol um ± 0,01% variiert, so sinken