Crystal Structure Investigation of Two Polymeric Chromium(III) Azide Complexes; $\text{KCr}(\text{pyridine})_4(\text{N}_3)_4$ and $\text{RbCr}(\text{pyridine})_3(\text{N}_3)_4$. A Structure Containing $\mu(1,3)$ and $\mu(1,1,3)$ Bridging Azido Ligands between Chromium and Rubidium Centered Polyhedra

M. A. S. Goher^a, M. A. M. Abu-Youssef^{b+}, F. A. Mautner^{b*}, and H. P. Fritz^b

^a Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426 Ibrahimia, Alexandria 21321, Egypt

^b Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Rechbauerstraße 12, A-8010 Graz, Austria

Z. Naturforsch. **47b**, 1754–1758 (1992); received June 22, 1992

Azide, Chromium, Crystal Structure, Pyridine Complexes, Potassium, Rubidium

The structures of two polymeric complexes of chromium(III) azide with pyridine, $\text{KCr}(\text{py})_4(\text{N}_3)_4$ (**1**), and $\text{RbCr}(\text{py})_3(\text{N}_3)_4$ (**2**), were determined by X-ray crystallography. Crystal data: **1**, $\text{C}_{20}\text{H}_{20}\text{N}_{16}\text{CrK}$, monoclinic, space group $\text{C}2/c$, $a = 1611.2(5)$, $b = 1050.6(3)$, $c = 1609.0(5)$ pm, $\beta = 91.69(3)^\circ$, $Z = 4$ and $R_w = 0.037$ for 923 diffractometer data; **2**, $\text{C}_{15}\text{H}_{15}\text{N}_{15}\text{CrRb}$, monoclinic, space group $\text{P}2_1/n$, $a = 1311.9(3)$, $b = 1139.0(4)$, $c = 1523.3(4)$ pm, $\beta = 109.39(2)^\circ$, $Z = 4$ and $R_w = 0.046$ for 2336 data.

The crystal structure of **1** contains six-coordinated chromium and potassium cations with two pyridine ligands and four $\mu(1,3)$ bridging azido groups forming a three-dimensional network structure. The chromium atoms are trans-coordinated by the pyridine ligands, whereas the potassium cations are *cis*-coordinated. The polymeric complex **2** features di- $\mu(1,1,3)$ azido bridged CrRbN_2 rings, distorted octahedral chromium(III) coordination geometry, seven-coordinated rubidium, and di- $\mu(1,3)$ azido bridges which link the binuclear $\text{RbCr}(\text{pyridine})_3(\text{N}_3)_2$ moieties into infinite chains parallel to the *b* axis.

Introduction

Chromium(III) normally shows a strong affinity for oxygen donors [1]. However, over the last two decades, extensive studies on chromium(III) complexes containing nitrogen donor ligands [2–7] have been reported. Despite this fact, very little attention was devoted to chromium(III) azide complexes [8, 9], and the one complex that has been studied by means of X-ray crystallography is $[\text{Cr}_4(\text{OH})_6(\text{en})_6](\text{N}_3)_6$ [10], in which the azide groups act as counter ions.

Recently we described the crystal structures of two chromium(III) azido complexes of pyridine, namely $\text{mer-}[\text{Cr}(\text{py})_3(\text{N}_3)_3]$ and $\text{NaCr}(\text{py})_4(\text{N}_3)_4$, where the chromium metal atom in both complexes is directly bonded to the azido groups [11]. The former meridional complex contains only terminal azido groups whereas the sodium complex possesses only $\mu(1,3)$ -bridging azido ligands. We now

report our investigation of the corresponding potassium and rubidium complexes. The present work constitutes part of our continuing study of metal pseudohalide complexes containing substituted pyridine ligands [12–14].

Experimental

Preparation, spectroscopic and magnetic data are given in [15].

X-ray crystallography

Single crystals of both compounds were measured at 300(1) K on a modified STOE 4-circle diffractometer. The cell dimensions were determined from setting angles of 39 (compound **1**) and 65 (compound **2**) reflections, respectively. Intensity data were collected with graphite monochromated $\text{MoK}\alpha$ radiation, ($\lambda = 71.069$ pm) and processed in the usual way (corrections: LP factor, absorption only for compound **1** [16], no extinction). Crystallographic data are given in Table I.

The structures were solved by the heavy-atom method. All non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were identified in difference maps and included in the refinement with isotropic displacement

⁺ On leave from Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

* Reprint requests to Dr. F. A. Mautner.

Compound	1	2
Chemical formula	C ₂₀ H ₂₀ N ₁₆ CrK	C ₁₅ H ₁₅ N ₁₅ CrRb
formula mass	575.6	542.9
Crystal system	monoclinic	monoclinic
Cell constants:		
<i>a</i>	1611.2(5) pm	1311.9(3) pm
<i>b</i>	1050.6(3) pm	1139.0(4) pm
<i>c</i>	1609.0(5) pm	1523.3(4) pm
β	91.69(3)°	109.39(2)°
<i>V</i>	2722(1) × 10 ⁶ pm ³	2147.1(9) × 10 ⁶ pm ³
Space group	C2/ <i>c</i>	P2 ₁ / <i>n</i>
<i>Z</i>	4	4
F(000)	1180	1084
Calculated density	1.404 Mg/m ³	1.679 Mg/m ³
Temperature	300(1) K	300(1) K
Approx. crystal dimensions	0.55 × 0.40 × 0.40 mm	0.40 × 0.25 × 0.22 mm
Data collection limits	2 θ < 43°; <i>hkl</i> : −16,0/16,10,16	2 θ < 60°; <i>hkl</i> : −18,0/18,16,21
Scan mode	ω -scan, $\Delta\omega$ = 1.5°	ω -scan, $\Delta\omega$ = 1.5°
$F_o > 4\sigma(F_o)$	923	2336
Least squares parameters	184	304
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 0.602 \text{ mm}^{-1}$	$\mu(\text{MoK}\alpha) = 2.75 \text{ mm}^{-1}$
<i>R</i>	0.037	0.079
<i>R_w</i>	0.037	0.046
Weighting function	1.000 $\sigma^{-2}(F_o)$	6.107 $\sigma^{-2}(F_o)$
Electron density in final ΔF map	0.23/−0.24 × 10 ^{−6} e/pm ³	0.84/−1.32 × 10 ^{−6} e/pm ³

Table I. Crystallographic data.

Table II. Atomic coordinates (×10⁴) and equivalent isotropic displacement factors (pm² × 10^{−1}) for **1**. U_{eq} was calculated as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
Cr	2500	2500	0	29(1)
K	0	187(2)	2500	53(2)
N 11	1619(3)	1130(4)	− 276(3)	43(3)
N 12	1480(3)	582(4)	− 913(3)	35(2)
N 13	1317(3)	1(5)	− 1532(3)	62(3)
N 21	3183(3)	1936(4)	− 1013(3)	45(3)
N 22	3772(3)	2522(4)	− 1313(2)	39(2)
N 23	4346(3)	3051(4)	− 1624(3)	61(3)
N 1	1839(2)	3868(3)	− 745(2)	33(2)
C 1	2244(3)	4686(5)	− 1267(3)	41(3)
C 2	1825(4)	5622(5)	− 1752(3)	51(4)
C 3	957(4)	5744(6)	− 1695(3)	54(4)
C 4	523(3)	4908(5)	− 1169(3)	55(4)
C 5	980(3)	3983(5)	− 712(3)	44(3)
N 2	9315(3)	1510(4)	8389(3)	47(3)
C 6	9307(3)	1406(5)	9229(3)	47(3)
C 7	8852(4)	2241(5)	9743(3)	58(4)
C 8	8375(3)	3214(6)	9383(4)	57(4)
C 9	8377(3)	3336(5)	8522(4)	59(4)
C 10	8851(3)	2477(6)	8054(3)	54(3)

Table III. Atomic coordinates (×10⁴) and equivalent isotropic displacement factors (pm² × 10^{−1}) for **2**. U_{eq} was calculated as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
Rb	3876(1)	359(1)	1639(1)	41(0)
Cr	2375(1)	− 2692(1)	139(1)	29(1)
N 11	1412(4)	− 3961(5)	304(4)	40(4)
N 12	1515(4)	− 4572(5)	963(4)	40(4)
N 13	1590(5)	− 5187(6)	1578(5)	64(5)
N 21	2335(4)	− 3358(5)	− 1094(4)	42(4)
N 22	1575(5)	− 3762(5)	− 1678(4)	38(4)
N 23	866(5)	− 4157(6)	− 2265(4)	66(5)
N 31	2465(4)	− 1923(5)	1353(3)	37(3)
N 32	1937(4)	− 2219(5)	1817(4)	34(4)
N 33	1465(4)	− 2463(5)	2298(4)	51(4)
N 41	3345(4)	− 1388(5)	6(4)	38(4)
N 42	3856(4)	− 1384(5)	− 502(4)	42(4)
N 43	4378(5)	− 1340(7)	− 974(5)	79(6)
N 1	998(4)	− 1711(5)	− 551(3)	30(3)
C 1	1043(5)	− 558(6)	− 611(5)	37(4)
C 2	181(5)	101(7)	− 1131(5)	49(5)
C 3	− 770(5)	− 428(7)	− 1611(5)	47(5)
C 4	− 826(5)	− 1618(7)	− 1545(5)	45(5)
C 5	63(5)	− 2234(6)	− 1004(4)	38(4)
N 2	3733(4)	− 3720(5)	773(4)	37(4)
C 6	3739(6)	− 4837(6)	556(6)	53(5)
C 7	4620(7)	− 5560(7)	939(6)	66(7)
C 8	5535(7)	− 5061(9)	1561(7)	68(7)
C 9	5541(6)	− 3904(8)	1800(6)	57(5)
C 10	4625(5)	− 3268(7)	1389(5)	42(5)
N 3	2787(5)	1907(6)	− 14(5)	62(5)
C 11	2070(7)	2693(8)	− 24(6)	61(6)
C 12	1424(7)	3251(8)	− 803(8)	75(8)
C 13	1563(7)	2988(9)	− 1624(7)	75(7)
C 14	2302(7)	2188(8)	− 1624(6)	68(7)
C 15	2905(6)	1675(8)	− 813(7)	66(7)

ment factors but with constraints applied to the positional parameters. The programs DIFABS [16] SHELX-76 [17], SHELXS-86 [18], THE XRAY SYSTEM [19] and PLATON [20] were used for computations on a μVAX 3100 computer. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [21]. The final positional parameters are listed in Table II and III. Se-

lected bond distances and bond angles are given in Table IV*.

* Further details on the structure determinations can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-W-7514 Eggenstein-Leopoldshafen 2, referring to the deposition number CSD 56345, the names of the authors, and the literature citation.

a) $\text{KCr}(\text{py})_4(\text{N}_3)_4$, (1):

K–N2b	255.6(5)	K–N13d	260.3(5)
K–N23a	257.2(5)	Cr–N11	206.1(4)
Cr–N1	213.5(4)	Cr–N21	207.9(4)
N11–N12	118.9(6)	N12–N13	119.1(7)
N21–N22	124.2(6)	N22–N23	119.9(6)
N2b–K–N13d	88.3(2)	N2b–K–N23a	90.3(1)
N2b–K–N2c	91.6(2)	N2b–K–N13e	85.7(2)
N2b–K–N23f	178.1(2)	N13d–K–N23a	93.8(2)
N13d–K–N2c	85.7(1)	N13d–K–N13e	171.3(2)
N13d–K–N23f	92.4(2)	N23a–K–N2c	178.1(2)
N23a–K–N13e	92.4(2)	N23a–K–N23f	87.9(2)
N11a–Cr–N1	88.9(2)	N11–Cr–N21a	89.5(2)
N11–Cr–N1	91.1(2)	N11–Cr–N11a	180.0(0)
N11–Cr–N21	90.5(2)	N1–Cr–N21	91.1(2)
Cr–N11–N12	129.4(4)	N11–N12–N13	177.1(5)
K–N13d–N12d	134.1(4)	Cr–N21–N22	126.3(3)
N21–N22–N23	177.6(4)	Ka–N23–N22	153.5(4)

Table IV. Selected bond distances (pm) and angles (deg).

Symmetry code: a: $1/2-x, 1/2-y, -z$; b: $1-x, -y, 1-z$; c: $-1+x, -y, -1/2+z$; d: $-x, -y, -z$; e: $x, -y, 1/2+z$; f: $-1/2+x, 1/2-y, 1/2+z$.

b) $\text{RbCr}(\text{py})_3(\text{N}_3)_4$, (2):

Rb–N3	301.7(7)	Rb–N13b	303.9(7)
Rb–N23c	292.9(7)	Rb–N31	313.6(5)
Rb–N33b	307.6(6)	Rb–N41	307.9(6)
Rb–N43a	301.0(8)	Cr–N11	199.0(6)
Cr–N1	208.7(5)	Cr–N2	208.3(5)
Cr–N21	201.0(5)	Cr–N31	201.4(5)
Cr–N41	200.9(5)	N11–N12	119.2(8)
N12–N13	114.8(9)	N21–N22	118.6(8)
N22–N23	114.7(9)	N31–N32	119.1(7)
N32–N33	113.9(8)	N41–N42	118.1(8)
N42–N43	114.6(10)		
N11–Cr–N1	88.4(2)	N1–Cr–N2	177.3(2)
N11–Cr–N2	90.8(2)	N11–Cr–N21	91.3(2)
N11–Cr–N31	92.6(2)	N11–Cr–N41	178.3(2)
N1–Cr–N21	88.9(2)	N31–Cr–N41	85.7(2)
N1–Cr–N31	90.4(2)	N1–Cr–N41	91.4(2)
N2–Cr–N21	88.5(2)	N2–Cr–N31	92.2(2)
N2–Cr–N41	89.4(2)	N21–Cr–N31	176.0(3)
N21–Cr–N41	90.4(2)	Rb–N31–Cr	109.9(2)
Rb–N41–Cr	112.2(2)	N11–N12–N13	177.6(8)
N21–N22–N23	177.3(7)	N31–N32–N33	176.3(7)
N41–N42–N43	177.0(7)		
Rb–N–N	6× from 120.1(4) to 165.2(5)		
Cr–N–N	4× from 123.6(4) to 129.1(5)		

Symmetry code: a: $1-x, -y, -z$; b: $1/2-x, 1/2+y, 1/2-z$; c: $1/2+x, -1/2-y, 1/2+z$; d: $1/2-x, -1/2+y, 1/2-z$; e: $-1/2+x, -1/2-y, -1/2+z$.

Discussion

The present study has shown complex **1** to be isotypic with the corresponding sodium complex $\text{NaCr}(\text{py})_4(\text{N}_3)_4$ [11]. The structural features of complex **1** (Table IV and Fig. 3 of ref. [11]) are very similar to those of $\text{Cd}(\text{py})_2(\text{N}_3)_2$ [22] and $\text{Mn}(\text{py})_2(\text{N}_3)_2$ [23] which are isomorphous. Each chromium or potassium cation is six-coordinated to four azido ligands and two pyridine molecules. These chromium and potassium octahedra are connected *via* $\mu(1,3)$ bridging azido ligands to form a three-dimensional network. Although the azide groups are almost linear within the experimental error (Table IV), the azide N11-N12-N13 is symmetrical ($\text{N11-N12} = 118.9(6)$ and $\text{N12-N13} = 119.1(6)$ pm) whereas the other (N21-N22-N23) is asymmetric ($\text{N21-N22} = 124.2(6)$ and $\text{N22-N23} = 119.9(6)$ pm). The Cr-N bond lengths lie in the range 206.1(4) to 213.5(4) pm, which is very close to that reported for the other chromium(III) complexes [24]. On the other hand, the K-N distances of 255.6(5) to 260.3(5) pm within the potassium octahedra (Table IV) are shorter than those in other KN_6 coordination octahedra [25–27].

The formulation $\text{RbCr}(\text{pyridine})_3(\text{N}_3)_4$ accurately represents the asymmetric unit in the polymeric structure **2** (Figs. 1 and 2). In this structure the chromium atom is surrounded by four azido groups (Cr-N from 199.0 to 201.4 pm) and two pyridine molecules (trans-conformation) at Cr-N bond lengths of 208.3(5) and 208.7(5) pm. Although the chromium atom is similar to that in compound **1** with distorted octahedral geometry,

the compounds are different in that two azido groups in **2** connect a rubidium atom at the same end giving rise to a ring CrRbN_2 . Each of these two azido groups further links a rubidium atom at the other end and is therefore functioning in the $\mu(1,1,3)$ mode. The chromium atom of each hetero binuclear RbCrN_2 unit is also coordinated by two asymmetric $\mu(1,3)$ bridging azido groups, whereas the rubidium atom is further coordinated by the end nitrogen of other two $\mu(1,1,3)$ and two $\mu(1,3)$ bridging azido groups and a pyridine molecule. These $\text{Cr-N}(\text{py})$ bond lengths match very closely the corresponding distances (208.5(2) and 209.5(2) pm) found in the structure of $[\text{Cr}(\text{py})_4\text{F}_2]^+$ [28]. Each rubidium atom, therefore, has an environment of six azido ligands (Rb-N from 292.9(7) to

Fig. 1. A perspective view showing both metal polyhedra in the complex **2**, $\text{RbCr}(\text{py})_3(\text{N}_3)_4$, with atom numbering scheme.

Fig. 2. Stereographic picture of the structure of complex **2**, $\text{RbCr}(\text{py})_3(\text{N}_3)_4$, viewed down the *b* axis.

313.6(5) pm) and a single nitrogen from the pyridine ligand at a Rb–N bond distance of 301.7(7) pm (Table IV). Seven and eight coordinated rubidium (with non-standard geometries) have been frequently encountered [29–31]. The Rb–N bond lengths resemble the corresponding values (from 291 to 323 pm) reported for other rubidium complexes [29–31]. Confirming the general characteristics of coordinated azides [32, 33], all azido groups are nearly linear and significant asymmetric (Table IV).

The $\mu(1,1,3)$ mode of azide bridging has previously been found in the structure of the polymeric complexes $\text{Cu}(\text{N}_3)_2$ [34–36], $\text{Cu}(\text{NH}_3)_2(\text{N}_3)_2$ [37],

$\text{Cu}(\text{py})_2(\text{N}_3)_2$ [38] and $\text{Cu}(\text{DENA})(\text{N}_3)_2$ (DENA = diethylnicotinamide) [12], whereas $\mu(1,3)$ bridging azide occurs in complexes $\text{Cd}(\text{py})_2(\text{N}_3)_2$ [22], $\text{Mn}(\text{py})_2(\text{N}_3)_2$ [23], $[\text{Cu}(\text{Ph}_3\text{P})_2\text{N}_3]_2$ [39], $[\text{Ni}_2(\text{tren})_2(\text{N}_3)_2]^{2+}$ where $\text{tren} = 2,2',2''$ -triamino-triethylamine [40], $[\text{Ni}(\text{Me}_4\text{cyclam})_2(\text{N}_3)_3]\text{I}$ [41] and $\text{Mn}(\text{acac})_2(\text{N}_3)$ [42]. To our knowledge complex **2** is the only example featuring the coexistence of di- $\mu(1,3)$ - and di- $\mu(1,1,3)$ -azido bridging in the same structure.

M. A. M. A. Y. thanks the Austrian Academic Exchange Service for scholarship. F. A. M. thanks Prof. Ch. Kratky for the use of equipment.

- [1] A. E. Martell and M. Calvin, *Chemistry of Metal Chelate Compounds*, p. 169, Prentice-Hall, New York (1952).
- [2] S. D. Sarma and B. D. Sarma, *Inorg. Chem.* **18**, 3618 (1979).
- [3] J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.* **82**, 4196 (1960).
- [4] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.* **6**, 1338 (1967).
- [5] C. D. Flint and A. P. Matthews, *Inorg. Chem.* **14**, 1008 (1975).
- [6] R. B. Wilson and E. I. Solomon, *Inorg. Chem.* **17**, 1729 (1978).
- [7] S. Decurtins and H. U. Güdel, *Inorg. Chem.* **21**, 3598 (1982).
- [8] H. E. Egghart, *J. Inorg. Nucl. Chem.* **43**, 1790 (1980).
- [9] S. I. Arzhankov and A. L. Poznyak, *Russ. J. Inorg. Chem.* **26**, 850 (1981).
- [10] M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.* **91**, 193 (1969).
- [11] M. A. S. Goher, M. A. M. Abu-Youssef, and F. A. Mautner, *Z. Naturforsch.* **47b**, 139 (1992).
- [12] M. A. S. Goher, R.-J. Wang, and T. C. W. Mak, *J. Mol. Struct.* **243**, 179 (1991).
- [13] M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* **99**, 223 (1990); *ibid.* **115**, 17 (1986).
- [14] F. A. Mautner and M. A. S. Goher, *Cryst. Res. Technol.* **25**, 1271 (1990).
- [15] H. P. Fritzner, M. A. S. Goher, M. A. M. Abu-Youssef, and K. Gatterer, *in press*.
- [16] N. Walker and D. Stuart, *Acta Crystallogr.* **A39**, 158, 1983.
- [17] G. M. Sheldrick, *SHELX-76*, A Program for Crystal Structure Determination, Cambridge (1976).
- [18] G. M. Sheldrick, *SHELX-86*, Program for the Solution of Crystal Structure, Göttingen (1986).
- [19] J. M. Stewart, *The X-RAY SYSTEM*. Version of 1976. Technical Report TR-446, University of Maryland (1976).
- [20] A. L. Spek, *Computational Crystallography*, p. 528, Clarendon Press, Oxford, UK (1982).
- [21] J. A. Ibers and W. C. Hamilton (eds): *International Tables for X-Ray Crystallography*, Vol. IV, pp. 99–149, Kynoch Press, Birmingham (1973).
- [22] I. Agrell, *Acta Chem. Scand.* **24**, 3575 (1975).
- [23] M. A. S. Goher and F. A. Mautner, *Croat. Chem. Acta* **63**, 559 (1990).
- [24] Y. Takeuchi and Y. Saito, *Bull. Chem. Soc. Jpn.* **29**, 319 (1957).
- [25] M. H. Bush, H. Luth, and M. R. Truter, *J. Chem. Soc. A*, 740 (1971).
- [26] P. L. Johnson, R. L. Musselman, and J. M. Williams, *Acta Crystallogr.* **B33**, 3155 (1977).
- [27] R. K. Brown, P. L. Johnson, T. J. Lynch, and J. M. Williams, *Acta Crystallogr.* **B34**, 1955 (1978).
- [28] G. Fochi, J. Strähle, and F. Gingl, *Inorg. Chem.* **30**, 4669 (1991).
- [29] N. S. Poonia and A. V. Bajaj, *Chem. Rev.* **79**, 389 (1979).
- [30] M. Doble and R. P. Phizackerly, *Acta Crystallogr.* **B30**, 2746 (1974).
- [31] J. Hasek and K. Huml, *Acta Crystallogr.* **B34**, 1812 (1978).
- [32] M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* **99**, 223 (1985).
- [33] Z. Dori and R. F. Ziolo, *Chem. Rev.* **73**, 247 (1973).
- [34] R. Söderquist, *Acta Crystallogr.* **B24**, 450 (1968).
- [35] I. Agrell and S. Lamnevik, *Acta Chem. Scand.* **22**, 2038 (1968).
- [36] I. Agrell, *Acta Chem. Scand.* **21**, 2647 (1967).
- [37] I. Agrell, *Acta Chem. Scand.* **20**, 1287 (1966).
- [38] I. Agrell, *Acta Chem. Scand.* **23**, 1667 (1969).
- [39] R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.* **10**, 1289 (1971).
- [40] C. G. Pierpont, D. N. Hendrickson, D. M. Doggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.* **14**, 604 (1975).
- [41] F. Wagner, M. T. Mocella, M. J. D'Aniello, A. H.-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.* **96**, 2625 (1974).
- [42] V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Am. Chem. Soc.* **96**, 2650 (1974).