Crystal structure of bis(trimethylphenylammonium) tetrabromocobaltate, $[\text{Me}_3\text{PhN}]_2[\text{CoBr}_4]$, and of bis(trimethylphenylammonium) tetrachlorocobaltate, $[\text{Me}_3\text{PhN}]_2[\text{CoCl}_4]$

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Abstract

$\text{C}_{18}\text{H}_{28}\text{Br}_4\text{CoN}_2$, monoclinic, $C12/c1$ (No. 15), $a = 15.994(3) \text{ \AA}$, $b = 9.780(2) \text{ \AA}$, $c = 31.354(4) \text{ \AA}$, $\beta = 94.46(1)^\circ$, $V = 4889.6 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.054$, $R_w(F^2) = 0.104$, $T = 293 \text{ K}$.

$\text{C}_{18}\text{H}_{28}\text{Cl}_4\text{CoN}_2$, monoclinic, $C12/c1$ (No. 15), $a = 15.542(2) \text{ \AA}$, $b = 9.552(2) \text{ \AA}$, $c = 30.860(5) \text{ \AA}$, $\beta = 95.45(1)^\circ$, $V = 4560.7 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.043$, $R_w(F^2) = 0.108$, $T = 293 \text{ K}$.

Source of material

Single crystals of the title compounds were obtained by slow evaporation of the solvent from an ethanolic solution of $[\text{PhMe}_3\text{N}]\text{Cl}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and an aqueous solution of $[\text{PhMe}_3\text{N}]\text{Br}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ in molar ratios of 2:1, respectively.

Discussion

Both compounds are isotypic and contain isolated $[\text{PhMe}_3\text{N}]^+$ cations and nearly regular tetrahedral $[\text{MX}_4]^{2-}$ anions. Bond length and angles are similar to those found in other chloro- and bromocobaltates(II) [1–6], but the range of the values in both compounds is smaller. Since distorted tetrahedral coordination geometries are due to hydrogen bonding [7, 8] the observation indicates the missing ability of the cation to form such bonds. In $[\text{PhMe}_3\text{N}]_2[\text{CoCl}_4]$ phase transitions were observed at 318 K and 331 K with enthalpies of transition of $\Delta_{\text{tr}}H = 12,70 \text{ kJ mol}^{-1}$ and $\Delta_{\text{tr}}H = 2.23 \text{ kJ mol}^{-1}$.

1. Bis(trimethylphenylammonium) tetrabromocobaltate, $[\text{Me}_3\text{PhN}]_2[\text{CoBr}_4]$

Table 1. Data collection and handling.

Crystal:	blue transparent plate, size 0.23 x 0.34 x 0.60 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	72.44 cm ⁻¹
Diffractometer, scan mode:	Siemens P4, $2\theta/\omega$
$2\theta_{\text{max}}$:	53.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5956, 4883
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2642
$N(\text{param})_{\text{refined}}$:	216
Program:	SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(12)	8f	0.3152(6)	-0.013(1)	0.3047(3)	0.110(7)
H(13)	8f	0.4589(7)	0.001(2)	0.2991(3)	0.110(7)
H(14)	8f	0.5257(6)	0.204(2)	0.2992(3)	0.110(7)
H(15)	8f	0.4497(6)	0.404(1)	0.3015(3)	0.110(7)
H(16)	8f	0.3062(5)	0.394(1)	0.3083(3)	0.110(7)
H(17)	8f	0.2122(5)	0.326(1)	0.3590(3)	0.110(7)
H(172)	8f	0.2141(5)	0.173(1)	0.3747(3)	0.110(7)
H(173)	8f	0.1292(5)	0.240(1)	0.3568(3)	0.110(7)
H(18)	8f	0.1843(6)	0.375(1)	0.2828(3)	0.110(7)
H(182)	8f	0.1026(6)	0.286(1)	0.2827(3)	0.110(7)
H(183)	8f	0.1696(6)	0.254(1)	0.2501(3)	0.110(7)
H(19)	8f	0.1955(6)	-0.010(1)	0.3226(4)	0.110(7)
H(192)	8f	0.1764(6)	0.024(1)	0.2740(4)	0.110(7)
H(193)	8f	0.1095(6)	0.056(1)	0.3066(4)	0.110(7)
H(22)	8f	0.0592(6)	0.778(1)	0.5347(3)	0.110(7)
H(23)	8f	-0.0440(8)	0.731(1)	0.5797(3)	0.110(7)
H(24)	8f	-0.1741(7)	0.666(1)	0.5529(4)	0.110(7)
H(25)	8f	-0.2002(6)	0.637(1)	0.4811(4)	0.110(7)
H(26)	8f	-0.0976(6)	0.678(1)	0.4355(3)	0.110(7)
H(27)	8f	0.1530(8)	0.739(2)	0.4982(4)	0.110(7)
H(272)	8f	0.1819(8)	0.738(2)	0.4516(4)	0.110(7)
H(273)	8f	0.1369(8)	0.610(2)	0.4692(4)	0.110(7)
H(28)	8f	0.0804(8)	0.952(2)	0.4772(4)	0.110(7)
H(282)	8f	0.0179(8)	0.952(2)	0.4361(4)	0.110(7)
H(283)	8f	0.1142(8)	0.931(2)	0.4320(4)	0.110(7)
H(29)	8f	0.0865(8)	0.737(2)	0.3937(4)	0.110(7)
H(292)	8f	-0.0099(8)	0.756(2)	0.3980(4)	0.110(7)
H(293)	8f	0.0339(8)	0.617(2)	0.4109(4)	0.110(7)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	8f	0.32124(6)	0.6918(1)	0.37058(3)	0.0344(6)	0.0550(7)	0.0510(6)	0.0004(5)	0.0031(4)	−0.0024(5)
Br(1)	8f	0.20586(5)	0.6625(1)	0.31765(3)	0.0425(5)	0.0821(7)	0.0688(6)	0.0044(5)	−0.0103(4)	−0.0096(5)
Br(3)	8f	0.30007(6)	0.9037(1)	0.40747(3)	0.0841(7)	0.0585(6)	0.0639(6)	0.0024(5)	0.0094(5)	−0.0085(5)
Br(4)	8f	0.32399(6)	0.5100(1)	0.42208(3)	0.0687(6)	0.0602(6)	0.0747(6)	−0.0035(5)	0.0003(5)	0.0145(5)
Br(5)	8f	0.44849(6)	0.6960(1)	0.33445(3)	0.0399(5)	0.1124(9)	0.0852(7)	−0.0033(6)	0.0186(4)	−0.0078(6)
N(1)	8f	0.2045(4)	0.1893(6)	0.3099(2)	0.043(4)	0.053(4)	0.047(4)	−0.001(3)	0.007(3)	−0.007(3)
C(11)	8f	0.2976(5)	0.1912(9)	0.3058(2)	0.045(5)	0.062(5)	0.032(4)	0.011(5)	0.002(3)	−0.009(4)
C(12)	8f	0.3418(6)	0.072(1)	0.3040(3)	0.066(6)	0.074(6)	0.058(5)	0.016(5)	0.011(4)	0.003(5)
C(13)	8f	0.4279(7)	0.081(2)	0.3009(3)	0.060(7)	0.13(1)	0.074(7)	0.045(8)	0.018(5)	−0.002(7)
C(14)	8f	0.4678(6)	0.201(2)	0.3006(3)	0.038(6)	0.15(1)	0.080(7)	0.010(8)	0.014(5)	0.002(8)
C(15)	8f	0.4229(6)	0.320(1)	0.3025(3)	0.053(6)	0.113(9)	0.088(7)	−0.019(7)	0.013(5)	−0.010(7)
C(16)	8f	0.3368(5)	0.314(1)	0.3059(3)	0.051(6)	0.071(7)	0.080(6)	−0.003(5)	0.011(5)	−0.009(5)
C(17)	8f	0.1886(5)	0.236(1)	0.3541(3)	0.051(5)	0.113(8)	0.053(5)	0.006(6)	0.016(4)	−0.011(5)
C(18)	8f	0.1615(6)	0.284(1)	0.2786(3)	0.058(6)	0.102(8)	0.068(6)	0.019(6)	−0.005(5)	0.013(6)
C(19)	8f	0.1684(6)	0.053(1)	0.3026(4)	0.061(6)	0.076(7)	0.123(9)	−0.010(6)	0.008(6)	−0.025(6)
N(2)	8f	0.0581(5)	0.764(1)	0.4534(2)	0.069(6)	0.098(7)	0.067(5)	0.011(5)	0.018(4)	0.013(5)
C(21)	8f	−0.0093(5)	0.7319(9)	0.4803(3)	0.045(5)	0.067(6)	0.057(5)	−0.002(4)	0.010(4)	0.006(4)
C(22)	8f	0.0067(6)	0.748(1)	0.5236(3)	0.070(7)	0.15(1)	0.051(6)	−0.041(7)	−0.003(5)	−0.005(6)
C(23)	8f	−0.0553(8)	0.721(1)	0.5503(3)	0.102(9)	0.16(1)	0.057(6)	−0.043(9)	0.029(6)	−0.020(7)
C(24)	8f	−0.1321(7)	0.682(1)	0.5346(4)	0.068(7)	0.108(9)	0.093(8)	−0.027(7)	0.033(6)	−0.027(7)
C(25)	8f	−0.1474(6)	0.665(1)	0.4921(4)	0.058(6)	0.085(7)	0.103(8)	−0.026(6)	−0.004(6)	−0.016(7)
C(26)	8f	−0.0862(6)	0.690(1)	0.4648(3)	0.061(6)	0.077(6)	0.058(5)	0.006(5)	−0.004(5)	−0.003(5)
C(27)	8f	0.1395(8)	0.708(2)	0.4695(4)	0.111(7)	0.20(1)	0.146(8)	0.025(7)	0.069(6)	0.052(7)
C(28)	8f	0.0685(8)	0.913(2)	0.4493(4)	0.111(7)	0.20(1)	0.146(8)	0.025(7)	0.069(6)	0.052(7)
C(29)	8f	0.0407(8)	0.714(2)	0.4104(4)	0.111(7)	0.20(1)	0.146(8)	0.025(7)	0.069(6)	0.052(7)

2. Bis(trimethylphenylammonium) tetrachlorocobaltate, [Me₃PhN]₂[CoCl₄]

Table 4. Data collection and handling.

Crystal:	deep blue, transparent plate, size 0.27 x 0.32 x 0.69 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	12.25 cm ^{−1}
Diffractometer, scan mode:	Siemens P4, 2 θ / ω
2 θ _{max} :	44°
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} :	3339, 2620
Criterion for I_{obs} , $N(hkl)$ _{gt} :	$I_{obs} > 2 \sigma(I_{obs})$, 2620
$N(param)$ _{refined} :	228
Program:	SHELXTL [9]

Table 5. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(12)	8f	0.3165(3)	−0.0151(6)	0.3064(2)	0.122(5)
H(13)	8f	0.4643(4)	−0.0041(7)	0.3017(2)	0.122(5)
H(14)	8f	0.5328(4)	0.2075(8)	0.2988(2)	0.122(5)
H(15)	8f	0.4556(4)	0.4111(7)	0.3022(2)	0.122(5)
H(16)	8f	0.3081(3)	0.4030(6)	0.3076(2)	0.122(5)
H(17)	8f	0.2135(4)	0.3270(7)	0.3618(2)	0.122(5)
H(18)	8f	0.2159(4)	0.1700(7)	0.3766(2)	0.122(5)
H(19)	8f	0.1279(4)	0.2392(7)	0.3591(2)	0.122(5)
H(20)	8f	0.1659(4)	0.2610(6)	0.2498(2)	0.122(5)
H(21)	8f	0.1781(4)	0.3833(6)	0.2838(2)	0.122(5)
H(22)	8f	0.0957(4)	0.2879(6)	0.2822(2)	0.122(5)
H(23)	8f	0.1731(4)	0.0204(6)	0.2741(2)	0.122(5)
H(24)	8f	0.1035(4)	0.0540(6)	0.3062(2)	0.122(5)
H(25)	8f	0.1915(4)	−0.0152(6)	0.3237(2)	0.122(5)
H(26)	8f	0.0646(4)	0.7569(8)	0.5362(2)	0.122(5)
H(27)	8f	−0.0438(5)	0.6954(8)	0.5789(2)	0.122(5)
H(28)	8f	−0.1793(4)	0.6453(7)	0.5476(2)	0.122(5)
H(29)	8f	−0.2032(4)	0.6358(7)	0.4732(2)	0.122(5)
H(30)	8f	−0.0974(4)	0.6976(6)	0.4303(2)	0.122(5)
H(31)	8f	0.1589(5)	0.760(1)	0.5012(3)	0.122(5)
H(32)	8f	0.1936(5)	0.762(1)	0.4552(3)	0.122(5)
H(33)	8f	0.1498(5)	0.627(1)	0.4716(3)	0.122(5)
H(34)	8f	0.0770(6)	0.9667(8)	0.4795(3)	0.122(5)
H(35)	8f	0.0169(6)	0.9655(8)	0.4357(3)	0.122(5)
H(36)	8f	0.1175(6)	0.9564(8)	0.4350(3)	0.122(5)
H(37)	8f	0.0500(8)	0.625(2)	0.4094(3)	0.122(5)
H(38)	8f	0.1015(8)	0.753(2)	0.3936(3)	0.122(5)
H(39)	8f	0.0009(8)	0.762(2)	0.3943(3)	0.122(5)

Table 6. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	8f	0.32323(4)	0.69391(7)	0.36917(2)	0.0378(4)	0.0515(4)	0.0459(4)	0.0018(3)	0.0063(3)	-0.0002(3)
Cl(1)	8f	0.21433(9)	0.6652(2)	0.31566(4)	0.0475(7)	0.085(1)	0.0703(8)	0.0066(7)	-0.0123(6)	-0.0103(7)
Cl(2)	8f	0.2990(1)	0.8979(1)	0.40423(4)	0.088(1)	0.0563(8)	0.0590(8)	0.0080(7)	0.0156(7)	-0.0068(6)
Cl(3)	8f	0.3226(1)	0.5200(1)	0.41926(4)	0.080(1)	0.0589(8)	0.0680(8)	-0.0051(7)	0.0073(7)	0.0134(7)
Cl(4)	8f	0.44953(9)	0.6977(2)	0.33774(5)	0.0444(7)	0.094(1)	0.090(1)	-0.0044(8)	0.0234(7)	-0.0089(9)
N(1)	8f	0.2031(2)	0.1920(4)	0.3112(1)	0.040(2)	0.052(2)	0.048(2)	0.004(2)	0.008(2)	-0.004(2)
C(11)	8f	0.2989(3)	0.1937(5)	0.3068(1)	0.039(2)	0.055(3)	0.037(2)	0.000(3)	0.008(2)	-0.003(2)
C(12)	8f	0.3443(3)	0.0709(6)	0.3054(2)	0.060(3)	0.063(3)	0.055(3)	0.012(3)	0.015(3)	-0.001(3)
C(13)	8f	0.4325(4)	0.0781(7)	0.3026(2)	0.059(4)	0.096(5)	0.068(4)	0.026(4)	0.016(3)	0.003(3)
C(14)	8f	0.4736(4)	0.2042(8)	0.3011(2)	0.041(3)	0.126(6)	0.058(3)	0.004(4)	0.013(3)	0.002(4)
C(15)	8f	0.4276(4)	0.3252(7)	0.3030(2)	0.051(3)	0.092(4)	0.076(4)	-0.014(3)	0.013(3)	-0.008(3)
C(16)	8f	0.3395(3)	0.3206(6)	0.3061(2)	0.050(3)	0.063(3)	0.066(3)	0.001(3)	0.011(3)	-0.005(3)
C(17)	8f	0.1888(4)	0.2359(7)	0.3562(2)	0.056(3)	0.115(5)	0.054(3)	0.000(3)	0.022(3)	-0.020(3)
C(18)	8f	0.1565(4)	0.2899(6)	0.2788(2)	0.052(3)	0.093(4)	0.070(4)	0.008(3)	-0.002(3)	0.017(3)
C(19)	8f	0.1643(4)	0.0501(6)	0.3031(2)	0.058(4)	0.070(4)	0.123(5)	-0.017(3)	0.007(4)	-0.022(4)
N(2)	8f	0.0647(3)	0.7769(5)	0.4525(1)	0.069(3)	0.085(3)	0.049(2)	0.015(3)	0.015(2)	0.007(2)
C(21)	8f	-0.0063(3)	0.7342(5)	0.4791(2)	0.054(3)	0.057(3)	0.049(3)	0.006(3)	0.008(3)	-0.003(2)
C(22)	8f	0.0100(4)	0.7334(8)	0.5233(2)	0.067(4)	0.137(6)	0.056(4)	-0.031(4)	0.003(3)	-0.004(4)
C(23)	8f	-0.0551(5)	0.6974(8)	0.5488(2)	0.094(5)	0.130(6)	0.054(3)	-0.030(5)	0.022(3)	-0.010(4)
C(24)	8f	-0.1349(4)	0.6652(7)	0.5304(2)	0.074(4)	0.081(4)	0.104(5)	-0.019(4)	0.035(4)	-0.008(4)
C(25)	8f	-0.1492(4)	0.6625(7)	0.4861(2)	0.057(4)	0.096(5)	0.109(5)	-0.010(4)	-0.002(4)	-0.015(4)
C(26)	8f	-0.0861(4)	0.6980(6)	0.4605(2)	0.067(4)	0.088(4)	0.061(3)	0.003(4)	-0.006(3)	-0.005(3)
C(27)	8f	0.1490(5)	0.727(1)	0.4718(3)	0.077(5)	0.172(8)	0.140(7)	0.043(6)	0.047(5)	0.052(6)
C(28)	8f	0.0694(6)	0.9294(8)	0.4505(3)	0.142(8)	0.105(6)	0.25(1)	0.026(6)	0.126(9)	0.080(7)
C(29)	8f	0.0534(8)	0.725(2)	0.4089(3)	0.19(1)	0.52(3)	0.080(6)	-0.16(2)	0.070(7)	-0.10(1)

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