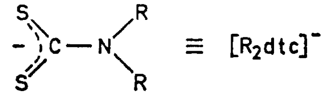
Synthesis and Properties of Dimeric Cobalt(III) Dithiocarbamate Complexes $[Co_2(R_2dtc)_5]^+$: *X*-Ray Structural Analysis of Pentakis(diethyldithiocarbamato)dicobalt(III) Tetrafluoroborate

By **Alan R. Hendrickson, Raymond L. Martin,*** and **Donald Taylor,** Research School of Chemistry, Australian National University, P.O. Box No. 4, Canberra, Australia 2600

The synthesis, properties, and structures of cationic dimeric dithiocarbamato-complexes (dtc) of cobalt(III) are described. The complexes $[Co_2(R_2dtc)_5]BF_4$ were prepared by reaction of $[Co(R_2dtc)_3]$ with boron trifluoride. The crystal structure of $[Co_2(Et_2dtc)_5]BF_4$ was determined from three-dimensional counter data. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 14.301(5), b = 16.819(3), c = 18.048(4) Å, and Z = 4. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares to R 0.092 for 1 141 independent reflections. The green-brown diamagnetic $[Co_2(R_2dtc)_5]^+$ species is comprised of an electrophilic $[Co(R_2dtc)_2]^+$ fragment co-ordinated in the *cis*-positions by sulphur atoms from an octahedral $[Co(R_2dtc)_3]$ molecule of opposite chirality. The lability of the bridging groups renders the dimer susceptible to attack by other nucleophiles and representative mixed chelates of the type $[Co(R_2dtc)_2(chel)]$ have been synthesised (chel = xanthate, dithiocarbamate, acetyl-, and dithioacetyl-acetonate).

INTEREST in the unsuspected capacity of the dithiocarbamate ligand (I) to stabilize complexes in unusually high oxidation states has lead to the isolation of dithiocarbamate complexes of Cu^{III}, Ni^{IV}, Fe^{IV}, and Mn^{IV}.[1-7]



(I)

For $[Co(R_2dtc)_3]$ oxidation of the $3d^6$ ion would be expected to be difficult. Indeed, preliminary electrochemical results confirm that these complexes are difficult to oxidize electrochemically[8] although the detailed nature of the oxidation process is still being studied.[9]

Chemical oxidation of dithiocarbamate complexes with BF_3 has afforded the well characterized Fe^{IV} salts, $[Fe(R_2dtc)_3]BF_4$ and Pasek and Straub suggested they also obtained the species $[Mn(Et_2dtc)_3]BF_4$ and $[Co(Et_2dtc)_3]BF_4$.[3] By a similar method $\{[Co(R_2dtc)_3]$ and $BF_3\}$, Gahan and O'Connor have extended the series of presumed Co^{IV} species, $[Co(R_2dtc)_3]BF_4$, and report unusual and unexpected properties, the complexes being diamagnetic and oligomeric with molecular complexities of 2—4 in chloroform.[10] These anomalies and the structure of the 'oxidized' cobalt species must be resolved before the electron-transfer behaviour of the cobalt dithiocarbamates can be interpreted. Accordingly, we have employed a BF_3 oxidation procedure, which has successfully provided complexes of Cu^{III}, Fe^{IV}, and Mn^{IV},[4] on the $[Co(R_2dtc)_3]$ species. In a preliminary communication[11] we summarized spectroscopic and other physicochemical evidence that the complexes we obtain should be formulated as diamagnetic dimers of Co^{III} *viz.*, $[Co_2(R_2dtc)_5]BF_4$ rather than derivatives of cobalt(IV).

EXPERIMENTAL

Preparation of Complexes.—Dithiocarbamate ligands were prepared by reaction of aqueous potassium hydroxide with carbon disulphide and the appropriate secondary amine. $[Co(R_2dtc)_3]$ compounds were prepared by reaction of cobalt(II) solutions with the ligand in the presence of oxygen. These complexes were recrystallized and gave satisfactory analyses. Commercial boron trifluoride diethyl etherate (45% Eastman Kodak) was used.

Pentakis(NN-*dibenzyldithiocarbamato*)*dicobalt*(III) *Tetrafluoroborate.*—$Et_2O{\cdot}BF_3$ (0.8 ml) was added to a saturated solution of $[Co\{(PhCH_2)_2dtc\}_3]$ in benzene (40 ml) at room temperature. Oxygen was bubbled in for 5 min, and the solution then set aside for 18 h. The resulting product was twice recrystallized by dissolving in CH_2Cl_2, adding Et_2O to the point of crystallization, and cooling to 0 °C.

The CCl_4 adduct of this complex was obtained by heating the cobalt dimer with CCl_4, to remove any $[Co\{(PhCH_2)_2dtc\}_3]$ and recrystallizing as before.

Pentakis(NN-*dialkyldithiocarbamato*)*dicobalt*(III) *Tetrafluoroborate,* $[Co_2(R_2dtc)_5]BF_4$.—The complexes [R = Me and cyclohexyl (C_6H_{11})] were prepared and purified by the above procedure.

Pentakis(NN-*dialkyldithiocarbamato*)*dicobalt*(III) *Tetrafluoroborate,*$[Co_2(R^1R^2dte)_5]BF_4$(R^1 = R^2 = Et, R^1 = Me, R^2 = Bu^n, R^1R^2 = pyrr).—These complexes were prepared similarly as above but purified by column chromatography on silica with benzene. The salts were eluted with acetone and recrystallized as before.

Pentakis(N-*methyl*-N-*n-butyldithiocarbamato*)*dicobalt*(III) *Tetraphenylborate.*—$NaBPh_4$ in ethanol was added dropwise with stirring to a solution of $[Co_2(Me,Bu^ndtc)_5]BF_4$ in ethanol, and the resulting precipitate of $[Co_2(Me,Bu^ndtc)_5]BPh_4$ washed and dried. Reaction of boron trifluoride gas with $[Co(Et_2dtc)_3]$ and $[Co\{C_6H_{11})_2dtc\}_3]$ under the conditions of

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ref.2 afforded samples of the dimers already described from the $Et_2O{\cdot}BF_3$ preparations.

Bis(NN-*dimethyldithiocarbamato*)(*chelate*)*cobalt*(III), [Co-$(Me_2dtc)_2$(chelate)].—(*a*) *Chelate* = NN-*dibenzyldithiocarbamate*. Potassium NN-dibenzyldithiocarbamate (0.31 g) in CH_2Cl_2 (25 ml) was added to $[Co_2(Me_2dtc)_5]BF_4$ (0.81 g) in CH_2Cl_2, and the product eluted from a silica column with toluene and recrystallized from dichloromethane–light petroleum (b.p. 80—100 °C).

(*b*) *Chelate* = NN-*dicyclohexyldithiocarbamate*. The complex was prepared from $K[(C_6H_{11})_2dtc]$ and $[Co_2(Me_2dtc)_5]BF_4$ in boiling acetone (3 min). The usual mixture of products obtained by evaporation of this solution were separated by column chromatography on silica with benzene. Addition of light petroleum (b.p. 80—100 °C) to the product in a minimum of benzene and subsequent cooling yielded the product as a benzene solvate. N.m.r. (CD_2Cl_2) confirms the presence of one molecule of benzene.

(*c*) *Chelate* = O-*n-propyldithiocarbonate*. This was prepared as described for $[Co(Me_2dtc)_2\{(PhCH_2)_2dtc\}]$ and separated from $[Co(Me_2dtc)_3]$ and KCl by preparative t.l.c. on silica with toluene. It was recrystallized from dichloromethane–light petroleum (b.p. 80—100 °C).

(*d*) *Chelate* = *acetylacetonate*. $[Co_2(Me_2dtc)_5]BF_4$ (0.81 g) and Na(acac) (0.12 g) were heated under reflux in toluene and the progress of reaction followed by t.l.c. At completion the solution was reduced to dryness under vacuum and the solid products separated by chromatography (dichloromethane and acetone) on silica. The product was recrystallized from dichloromethane–light petroleum.

(*e*) *Chelate* = *dithioacetylacetonate* = $[sacsac]^-$. A methanolic solution (40 ml) of sodium dithioacetylacetonate[12] (1.3mM) was allowed to react with $[Co_2(Me_2dtc)_5]BF_4$ (1.1-mM) in methanol–acetone (3 : 4, 75 ml) at room temperature. Purification was accompanied by column chromatography and preparative t.l.c. on silica with benzene as eluant. The product was recrystallized from dichloromethane by addition of methanol followed by cooling (0.2 g).

CRYSTALLOGRAPHY

Single crystals of $[Co_2(Et_2dtc)_5]BF_4$ suitable for *X*-ray analysis were grown from ethanol–dichloromethane–diethyl ether. A single crystal in the form of a prism with perpendicular distances (cm) between crystal faces of 0.0178 for [110] and [$\bar{1}\bar{1}0$], 0.0180 for [$1\bar{1}0$] and [$\bar{1}10$], and 0.0228 for [001] and [$00\bar{1}$] was mounted on a quartz fibre with Araldite. Preliminary Weissenberg and precession photographs established the crystal class and space group. The diffracted *X*-ray intensities were severely attenuated at even moderate Bragg angles ($\sin\theta/\lambda > 0.30$), indicative of high thermal motion in the crystal or possible atomic disorder.

The crystal was then transferred to a Picker FACS 1 four-circle diffractometer with the crystallographic *c* axis approximately collinear with the instrumental ϕ axis. The crystal orientation matrix and unit-cell dimensions were obtained from least-squares refinement[13] of the 2θ, ω, χ, and ϕ setting angles of 12 carefully centred reflections in the range $44° \leqslant 2\theta \leqslant 56°$ (graphite crystal monochromator, Cu-$K_{\alpha 1}$ radiation, $\lambda = 1.5405$ Å, take-off angle 2.0°, temperature 21 ± 1 °C).

Crystal Data.—$C_{25}H_{50}BCo_2F_4N_5S_{10}$, $M = 946.02$, Orthorhombic, $a = 14.301(5)$, $b = 16.819(3)$, $c = 18.048(4)$ Å, $U = 4341.2$ Å^3, $D_m = 1.44$ g cm^{-3} (flotation) $Z = 4$, $D_c = 1.45$ g cm^{-3}. Space group $P2_12_12_1$ (D_2^4, No. 19) from systematic absences $h00$ $h = 2n + 1$, $0k0$ $k = 2n + 1$, and $00l$ $l = 2n + 1$.[14] Cu-K_α radiation, μ(Cu-K_α) = 108.15 cm^{-1}.

Data Collection.—The intensities of reflections of the forms hkl and $h\bar{k}l$ in the range $3° \leqslant 2\theta \leqslant 120°$ were measured by the θ—2θ scan technique by use of monochromated Cu-K_α radiation, take-off angle 3°. Each reflection was scanned from 1.1° below the K_{α_1} peak to 1.1° above the K_{α_2} peak (2θ scan speed 2° min^{-1}) accumulating p counts in t_p seconds. Stationary counter background counts (b_1,b_2) were measured at the limits of the scan range for a total time (t_b) of 20 s. The intensities of 3 standard reflections [indices (0,5,4), (6,0,6), and (0,−8,0)] monitored every 100 reflections decreased by 4.49, 3.52, and 3.56% during data collection. The decay was assumed to be linear and 2θ independent. A total of 7 761 reflections including standards was measured.

The reflection intensities were corrected for anisotropic decay[15] and for Lorentz-polarization effects. Reflections for which the individual background measurements differed significantly were removed from the data. Assuming a linear variation of the background intensity over the scan range, the nett integrated intensity (I) and standard deviation $\sigma(I)$ were calculated according to $I = p - (t_p/t_b)(b_1 + b_2)$ and $\sigma(I) = [p + (t_p/t_b)^2(b_1 + b_2)]^{\frac{1}{2}}$. Structure-factor amplitudes and standard deviations were calculated from $F_0 = (I/LP)^{\frac{1}{2}}$ and $\sigma(F_o) = \{[\sigma(I)/LP]^2 + [\rho F_o{}^2]^2\}^{\frac{1}{2}}/2F_o$ where $\rho[= (0.002)^{\frac{1}{2}}]$ is an arbitrary constant to account for instrumental instability and $LP = (\cos^2 2\theta + \cos^2 2\theta_m)/\sin 2\theta$, θ and θ_m being the Bragg angles for the reflection and monochromator respectively.[16,17] Unobserved reflections [$I/\sigma(I) < 3.0$] were discarded and the remaining data were sorted and equivalent reflections averaged according to *mmm* point-group symmetry. The statistical *R* factor was 0.039 for the 1 141 independent reflections.

Solution and Refinement of Structure.—A three-dimensional Patterson function was solved for the co-ordinates of the two independent cobalt atoms. Because of the proximity of the cobalt atoms to the ($\frac{1}{4}$, y, z) plane, the atoms were initially constrained to that plane, and the derived Fourier synthesis exhibited sulphur atom peaks plus those of their mirror images. One sulphur atom [S(11)] was added to the phasing atom set to break the pseudosymmetry and the positions of the remaining nine sulphur atoms were determined from a Fourier synthesis. The cobalt atoms were then relocated in general positions from a difference-Fourier phased only by the sulphur atoms. The remaining non-hydrogen atoms were located from successive difference Fouriers although difficulty was encountered with the β-carbon atoms of some ethyl groups. The structure was then refined by block-diagonal least-squares techniques [the function minimized being $\Sigma w(|F_o| - |F_c|)^2$] with isotropic temperature factors for all non-hydrogen atoms until convergence at *R* 0.130

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and R' 0.135 $\{R' = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. Individual reflection weights were assigned as $\sigma(F_o)^{-2}$. Data were then corrected for absorption effects by an analytical method [transmission range 0.392—0.540], sorted, and reaveraged. In view of the lack of significant difference between Bijvoet pairs of the form (hkl) and $h\bar{k}l)$, and the requirement of the structural analysis only to establish the chemical identity and stereochemistry of the complex, the data were all averaged to the (hkl) form and the question of the absolute configuration was not pursued. Atomic scattering factors were taken from ref. 18 and were corrected only for the real part of the anomalous scattering.[19] Anisotropic temperature factors of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ were introduced for the cobalt, sulphur, and fluorine atoms and refinement continued until convergence at R 0.092 and R' 0.060. In the final cycle, all changes in atomic parameters were $<0.3\sigma$.

TABLE 1

Atomic positional and thermal parameters, with estimated standard deviations in parentheses

(a) Positional and anisotropic thermal parameters ($\times 10^4$)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	2 542(3)	1 679(2)	1 458(2)	88(3)	46(2)	43(2)	6(3)	−6(3)	−16(2)
Co(2)	2 478(3)	551(2)	−85(2)	86(3)	44(2)	32(2)	−10(3)	9(3)	−18(2)
S(11)	3 234(5)	520(4)	1 059(4)	88(5)	45(3)	66(4)	−4(5)	−4(4)	−11(3)
S(12)	1 658(5)	719(4)	1 994(4)	91(6)	62(4)	55(4)	11(5)	19(4)	−10(3)
S(21)	1 805(5)	1 734(4)	331(4)	106(6)	57(4)	38(3)	−4(4)	11(4)	−7(3)
S(22)	3 428(6)	2 534(4)	788(4)	123(7)	48(4)	63(4)	−11(5)	−23(5)	−5(3)
S(31)	1 722(5)	2 652(4)	2 035(4)	123(7)	66(4)	60(4)	40(5)	−10(5)	−18(3)
S(32)	3 402(5)	1 919(4)	2 489(4)	86(6)	79(4)	60(4)	32(5)	−21(4)	−13(3)
S(41)	3 822(5)	997(4)	−581(4)	99(6)	43(3)	67(4)	−3(4)	14(4)	−4(3)
S(42)	3 213(5)	−548(4)	−461(4)	130(7)	51(4)	64(4)	−8(5)	30(5)	−13(3)
S(51)	1 148(5)	−92(4)	219(4)	106(6)	81(4)	33(3)	−23(5)	8(4)	−15(3)
S(52)	1 637(5)	572(4)	−1 141(4)	109(6)	90(5)	40(3)	−50(6)	11(4)	5(3)
F(1)	1 718(12)	3 300(11)	7 148(9)	161(15)	147(13)	94(10)	19(13)	9(11)	54(10)
F(2)	2 585(14)	3 478(16)	6 252(10)	161(17)	316(25)	88(11)	16(20)	−4(12)	36(13)
F(3)	3 132(12)	3 083(11)	7 204(10)	205(19)	151(14)	100(11)	78(15)	5(12)	21(10)
F(4)	2 682(16)	4 199(12)	7 200(17)	259(24)	117(13)	341(27)	−79(17)	148(22)	−88(16)

(b) Positional ($\times 10^4$) and isotropic thermal parameters

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
C(1)	2 385(16)	19(11)	1 682(10)	4.0(5)
N(1)	2 413(13)	−738(10)	1 801(9)	6.6(5)
C(111)	3 133(20)	−1 292(17)	1 427(17)	12.1(10)
C(112)	4 034(17)	−1 381(15)	1 885(14)	8.8(8)
C(121)	1 721(18)	−1 053(16)	2 417(14)	9.5(8)
C(122)	821(19)	−1 293(16)	2 003(15)	10.6(9)
C(2)	2 568(17)	2 410(13)	122(12)	6.6(6)
N(2)	2 602(14)	2 871(11)	−517(11)	8.2(6)
C(211)	1 871(18)	2 710(15)	−1 129(14)	8.7(8)
C(212)	1 084(18)	3 318(15)	−1 051(13)	7.8(7)
C(221)	3 377(18)	3 512(15)	−652(14)	9.5(8)
C(222)	4 244(19)	3 156(16)	−1 050(14)	9.5(9)
C(3)	2 622(19)	2 549(14)	2 661(13)	8.4(7)
N(3)	2 478(16)	3 025(12)	3 310(11)	9.5(6)
C(311)	1 714(19)	3 608(15)	3 493(15)	10.4(9)
C(312)	2 052(19)	4 425(17)	3 370(16)	12.3(11)

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
C(321)	3 300(20)	2 993(16)	3 831(15)	10.0(9)
C(322)	2 989(20)	2 477(19)	4 503(18)	13.9(11)
C(4)	3 996(18)	47(14)	−801(13)	8.0(8)
N(4)	4 874(14)	−208(12)	−1 119(11)	8.0(6)
C(411)	5 618(18)	421(15)	−1 327(14)	9.0(9)
C(412)	6 378(20)	424(17)	−735(16)	11.4(10)
C(421)	4 874(21)	−1 160(19)	−1 353(18)	13.3(11)
C(422)	5 280(21)	−1 463(20)	−718(18)	13.7(11)
C(5)	797(16)	41(13)	−670(12)	6.6(7)
N(5)	92(13)	−269(11)	−1 001(10)	6.5(6)
C(511)	−672(17)	−663(16)	−531(15)	9.3(8)
C(512)	−447(18)	−1 547(17)	−554(16)	11.0(9)
C(521)	−128(19)	−171(17)	−1 855(14)	9.7(9)
C(522)	−731(20)	552(18)	−1 844(15)	11.4(10)
B	2 512(31)	3 647(26)	6 934(25)	15.7(15)

A final difference-Fourier exhibited residual electron density in the range −0.6 to 1.0 eÅ^{-3}, with the largest positive peaks within 0.1 Å of the cobalt atoms. Hydrogen atoms were not located. The standard deviation of an observation of unit weight, defined as $\{\Sigma w(|F_o| - |F_c|)^2/(m-n)\}^{\frac{1}{2}}$ where m is the number of observations and n the number of variables (269) was 2.87. Final atomic positional and thermal parameters are given in Table 1 together with their estimated standard deviations derived from inversion of the block-diagonal matrices. Selected bond lengths and angles are given in Table 2, and final observed and calculated structure factors are deposited as Supplementary Publication No. SUP 21411 (6 pp., 1 microfiche).* All calculations were carried out on a UNIVAC 1108 computer at the Australian National University Computer Centre with programmes described elsewhere,[20] except for the analytical absorption correction [21] programme TOMPA modified (by J. D. Bell) for the Picker diffractometer geometry, and the data reduction programme SETUP 3 (P. O. Whimp).

RESULTS AND DISCUSSION

The cobalt dimers are readily prepared in the presence of $Et_2O{\cdot}BF_3$, presumably *via* an oxidation pathway. In view of their possible alternative formulations, complete analytical data have been obtained (Table 3), leaving no doubt that the species should be formulated at least as a dimer; $[Co_2(R_2dtc)_5]BF_4$.

Not unexpectedly, the mass spectrum of $[Co_2(Me_2dtc)_5]$-BF_4 does not contain a parent-ion peak. The highest

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

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[21] J. de Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

value m/e peaks at 419 and 299 correspond to $[\mathrm{Co(Me_2dtc)_3}]^+$ and $[\mathrm{Co(Me_2dtc)_2}]^+$ respectively.

TABLE 2

Selected interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

n	1	2	3	4	5
Co(1)–S(*n*1)	2.301(8)	2.294(8)	2.266(8)		
Co(1)–S(*n*2)	2.266(8)	2.268(8)	2.266(9)		
Co(2)–S(*n*1)	2.331(8)	2.335(8)		2.248(8)	2.254(8)
Co(2)–S(*n*2)				2.231(8)	2.256(9)
C(*n*)–S(*n*1)	1.86(2)	1.62(2)	1.72(3)	1.67(3)	1.70(2)
C(*n*)–S(*n*2)	1.67(2)	1.73(3)	1.57(3)	1.62(3)	1.72(2)
C(*n*)–N(*n*)	1.29(3)	1.39(3)	1.43(3)	1.44(3)	1.28(3)
N(*n*)–C(*n*11)	1.54(3)	1.54(3)	1.51(4)	1.55(3)	1.53(3)
N(*n*)–C(*n*21)	1.58(3)	1.57(3)	1.51(3)	1.65(4)	1.58(3)
C(*n*11)–C(*n*12)	1.54(4)	1.53(4)	1.48(4)	1.52(4)	1.52(4)
C(*n*21)–C(*n*22)	1.54(4)	1.55(4)	1.56(4)	1.38(5)	1.49(4)
B–F(*n*)	1.35(5)	1.26(5)	1.40(5)	1.06(5)	

(*b*) Bond angles

S(11)–Co(1)–S(12)	76.7(3)	S(11)–Co(1)–S(21)	87.4(3)
S(21)–Co(1)–S(22)	76.0(3)	S(11)–Co(2)–S(21)	85.7(3)
S(31)–Co(1)–S(32)	77.0(3)	Co(1)–S(11)–Co(2)	93.4(3)
S(41)–Co(2)–S(42)	75.7(3)	Co(1)–S(21)–Co(2)	93.5(3)
S(51)–Co(2)–S(52)	76.3(3)	C(1)–S(11)–Co(2)	104.1(7)
		C(2)–S(21)–Co(2)	104.2(9)

(*c*) Non-bonded contacts <3.5 Å

Co(1) · · · Co(2)	3.372(5)	C(312) · · · F(4^{III})	3.15(4)
S(11) · · · S(21)	3.17(1)	C(421) · · · F(3^{IV})	3.48(4)
C(112) · · · F(1^{I})	3.43(3)	C(422) · · · F(2^{IV})	3.21(4)
C(121) · · · F(3^{I})	3.44(3)	C(511) · · · F(2^{V})	3.36(3)
C(122) · · · F(3^{I})	3.39(3)	C(512) · · · F(2^{V})	3.30(3)
C(211) · · · F(1^{II})	3.27(3)	C(512) · · · F(1^{V})	3.41(3)
C(121) · · · F(1^{II})	3.38(3)	C(521) · · · F(1^{V})	3.47(3)

Transformations of the asymmetric unit x, y, z are defined by Roman numeral superscripts:

I $\frac{1}{2} - x, -y, z - \frac{1}{2}$
II $x, y, z - 1$
III $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$
IV $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
V $-x, y - \frac{1}{2}, \frac{1}{2} - z$

The i.r. spectra (KBr disc, 1 600—300 cm^{-1}) of the new compounds are similar to those of their tervalent monomeric precursors. Additional sharp bands at 521 and 532 cm^{-1} and a broad band centred at 1 070 cm^{-1} confirm the presence of $\mathrm{BF_4}^-$. The only band to show a significant shift in energy is the $\gamma(\mathrm{C \overset{\cdots}{-} N})$ band which moves 15—19 cm^{-1} to higher energies in the dimer; *cf.*, $[\mathrm{Co_2(R^1R^2dtc)_5}]\mathrm{BF_4}$ and $[\mathrm{Co(R^1R^2dtc)_3}]$; $\mathrm{R^1 = R^2 = Me}$: 1 540, 1 525; $\mathrm{R^1 = R^2 = Et}$: 1 510, 1 495; R = pyrr: 1 504, 1 485; $\mathrm{R^1 = R^2 = PhCH_2}$: 1 497, 1 480, and $\mathrm{R^1 = Me}$, $\mathrm{R^2 = Bu^n}$: 1 520, 1 502 cm^{-1}. Such a shift is usually observed on increasing the oxidation state of the metal (*i.e.*, increasing the positive charge shared by a set number of ligands) but in the present example this shift is ascribed to the decrease in the number of ligands sharing the same positive charge. However, the presence of bridging ligands in the dimer may also modify the $\gamma(\mathrm{C \overset{\cdots}{-} N})$ frequency. The presence of a peak at 785 cm^{-1} in the spectrum of the $\mathrm{CCl_4}$ solvate of $[\mathrm{Co_2\{(PhCH_2)_2dtc\}_5}]\mathrm{BF_4}$ which is not present in that of the non-solvate is ascribed to $\mathrm{CCl_4}$.

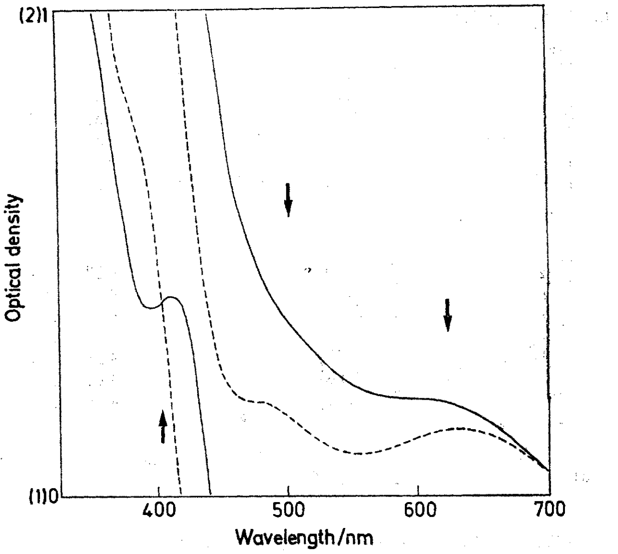

FIGURE 1 Electronic spectra of $\mathrm{Co^{III}}$ complexes in $\mathrm{CH_2Cl_2}$. Molar extinction coefficients are included in Table 4; dashed line $[\mathrm{Co(Me_2dtc)_3}]$, full line $[\mathrm{Co_2(Me_2dtc)_5}]\mathrm{BF_4}$

The electronic spectra of the dimers and of their monomeric precursors are presented in Table 4. Except for subtle changes in peak positions and intensities (Figure 1)

TABLE 3

Analytical data for the cobalt dimers, $[\mathrm{Co_2(R_2dtc)_5}]\mathrm{BF_4}$, and mixed-ligand complexes, $[\mathrm{Co(Me_2dtc)_2(chelate)}]$

Compound	Analysis (%) [a]						
$\mathrm{R^2}$	Co	B	F	C	H	S	N
$\mathrm{Me_2}$	14.4 (14.6)	1.4 (1.3)	9.7 (9.4)	21.7 (22.4)	3.8 (3.8)	39.8 (39.8)	8.6 (8.7)
$\mathrm{Et_2}$	12.5 (12.5)	1.1 (1.1)	8.2 (8.0)	31.9 (31.7)	5.3 (5.3)	34.0 (33.9)	7.2 (7.4)
pyrr	12.4 [b] (12.6)	1.1 (1.2)	7.8 (8.1)	32.0 (32.1)	4.4 (4.3)	34.4 (34.3)	7.3 (7.5)
Me, $\mathrm{Bu^n}$	11.2 (11.6)	1.0 (1.1)	7.2 (7.5)	36.8 (35.5)	6.6 (6.0)	31.0 (31.6)	6.5 (6.9)
$\mathrm{(PhCH_2)_2}$	7 .9 (7.5)	0.7 (0.7)	4.8 (4.9)	57.7 (57.5)	4.6 (4.5)	20.5 (20.5)	4.3 (4.5)
$\mathrm{(PhCH_2)_2}$ [c]	6.6 (6.9)	0.9 (0.6)	5.6 (4.4)	53.4 (53.1)	4.3 (4.1)	18.3 (18.6)	4.1 (4.1)
Me, $\mathrm{Bu^n}$ [d]	9.4 (9.4)	0.8 (0.9)		49.3 (51.9)	6.2 (6.5)	21.9 (25.7)	5.7 (5.6)
$\mathrm{(C_6H_{11})_2}$		0.7 (0.7)	4.7 (5.1)	52.0 (52.5)	7.5 (7.5)		5.0 (4.7)
Chelate							
$\mathrm{(PhCH_2)_2dtc}$				44.0 (44.1)	4.7 (4.6)		7.0 (7.4)
$\mathrm{(C_6H_{11})_2dtc}$ [e]				48.7 (47.4)	6.2 (6.4)		6.7 (6.6)
$\mathrm{Pr^nOCS_2}$				27.8 (27.6)	4.5 (4.4)		6.6 (6.4)
acac				32.4 (33,2)	4.7 (4.8)		6.4 (7.0)
sacsac				30.2 (30.7)	4.6 (4.5)		6.5 (6.5)

[a] Calculated values in parentheses. [b] Mean of three. [c] With one mol $\mathrm{CCl_4}$; Found: Cl, 8.3. Calc. Cl, 8.2%. [d] $\mathrm{BPh_4}$ salt. [e] Complex contains one mol $\mathrm{C_6H_6}$.

the spectra are quite similar, in accord with both species being six-co-ordinate Co^{III} complexes with dithiocarbamate ligands (*vide supra*).

TABLE 4

Electronic spectra of $[Co(R_2dtc)_3]$ and $[Co_2(R_2dtc)_5]X$ compounds [a]

Compound	Absorption maxima (nm)		Extinction coefficients (log ε)
(*a*) $[Co(R_2dtc)_3]$			
R_2			
Me_2	641 (2.69)	476 (2.83)	386 (3.92)
Et_2	643 (2.72)	477 (2.88)	356 (4.15)
Me, Bu^n	641 (2.72)	476 (2.95)	358 (4.13)
$(PhCH_2)_2$	640 (2.76)	482 (2.96)	355 (4.13)
pyrr	651 (2.65)	483 (2.81)	389 (3.91)
pyrr, $CHCl_3$	651 (2.68)	482 (2.83)	389 (3.93)
(b) $[Co_2(R_2dtc)_5]BF_4$			
R_2			
Me_2	622 (3.09)	[b]	412 (4.14)
Et_2	617 (3.16)	[b]	414 (4.22)
Me, Bu^n	614 (3.13)	[b]	409 (4.18)
Me, Bu^n [c]	610 (3 19)	[b]	408 (4.19)
$(PhCH_2)_2$	616 (3.22)	[b]	418 (4.24)
$(PhCH_2)_2CCl_4$	613 (3.18)	[b]	417 (4.23)
pyrr	631 (3.07)	[b]	408 (4.16)
$(C_6H_{11})_2$	619	[b]	426

[a] CH_2Cl_2 solutions [b] Appears to be a weak underlying peak around 516 nm. [c] X = BPh_4.

Conductance measurements (Figure 2) on $[Co_2(Me_2dtc)_5]BF_4$ in nitromethane over the concentration range 8×10^{-5}—2×10^{-2}M suggest that there is little ion-pairing of the 1 : 1 electrolyte in this solvent. Calibration runs on $[Bu^n_4N]BPh_4$ and $[Et_4N]BF_4$, also in nitromethane, were in agreement with literature studies.[22,23] The conductivities of the remaining dimers were measured on *ca.* 10^{-3}M-solution with the BF_4 salts yielding similar results to the dimethyldithiocarbamate derivative (Table 5). The smaller conductance of $[Co_2(Me,Bu^ndtc)_5]BPh_4$ reflects the lower λ_0 value for the BPh_4^- ion.[24]

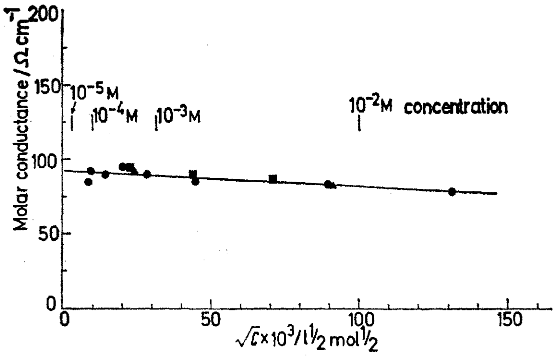

FIGURE 2 Dependence of the molar conductance of $[Co_2(Me_2dtc)_5]BF_4$ on its concentration in nitromethane. Symbols represent three independent dilution series

Molecular-weight measurements by vapour pressure osmometry were obtained in a variety of solvents (Table 5). In nitromethane, where little ion-pairing takes place (conductance results), the measurements agree with the dimeric formulation if allowance is made for *ca.* 10% ion-pairing at *ca.* 10^{-2} M. In CH_2Cl_2 however, $[Co_2(Me_2dtc)_5]BF_4$ at 0.017M is almost 90% ion-paired, illustrating the dramatic solvent dependence of colligative properties.

TABLE 5

Molecular weight and conductance data on $[Co_2(R_2dtc)_5]BF_4$ species

Complex R_2	Molecular-weight data [a] *M*	I.P. (%) [c]	Conc./mol	Solvent	Temp./°C	Conductance [b] Λ_M [d]
Me_2	433	7.4	0.018	$MeNO_2$	37	89 [e]
Me_2	760	88.6	0.017	CH_2Cl_2	25	
Et_2	488	3.2	0.009	$MeNO_2$	37	85
pyrr	517	10.5	0.011	$MeNO_2$	37	78
Me, Bu^n	523	3.0	0.009	$MeNO_2$	37	71
Me, Bu^n [f]						49
$(PhCH_2)_2$	809	3.2	0.010	$MeNO_2$	37	77
$(PhCH_2)_2$	970	23.7	0.0012	$CHCl_3$	35.4	
$(PhCH_2)_2$	790	0.8	0.0006	$CHCl_3$	35.4	
$(PhCH_2)_2$,CCl_4	698	21.8	0.009	$MeNO_2$	37	109

[a] By vapour-pressure osmometry. [b] Nitromethane solutions at *ca.* 10^{-3}M at 25.0 °C. [c] % Ion pairing: 100 (MWt — Complete Dissn. MWt)/Complete Dissn. MWt. [d] Molar conductance (cm^2 mol^{-1} ohm^{-1}). [e] See Figure 2 for concentration dependence of Λ_M. [f] BPh_4 salt.

Although these findings, together with n.m.r. (*vide infra*) suggested various dimeric structures,[11] a single-crystal *X*-ray study was required to differentiate between these possibilities and unequivocably establish the dimeric formulation. The cation $[Co_2(Et_2dtc)_5]^+$ (Figure 3) may be considered as a $[Co(Et_2dtc)_3]$ unit co-ordinated in the *cis* positions of an octahedral $[Co(Et_2dtc)_2]^+$ species of opposite chirality. The Co_2S_{10} core has approximate C_2 symmetry with the rotation axis collinear with the Co(1) · · · Co(2) vector. The Co(1) · · · Co(2) distance, 3.372(5) Å, precludes any significant metal–metal bonding.

The geometry of the CoL_3 unit is quite similar to that found for $[Co(Et_2dtc)_3]$,[25,26] the mean Co(1)–S(non-bridging) bond distance (2.266 Å) and mean S(*n*1)–Co(1)–S(*n*) angle (76.6°) agreeing closely with values (2.26 Å and 76.2°) in the tris-complex. The Co(1)–S(bridging) bond lengths average 2.298 Å, an increase of *ca.* 0.03 Å. This lengthening is a result of the shared co-ordination of these sulphur atoms to Co(1) and Co(2). The mean Co(2)–S(non-bridging) sulphur bond lengths are 2.247 Å, marginally shorter than in the CoL_3 unit. The Co(2)–S(bridging) distances (2.333 Å) are the longest observed in this structure. This finding is reflected in the facile rupture of these bonds when the dimer is allowed to react with other ligands (*vide infra*). The dithiocarbamate 'bite' distances average 2.80 Å and nearest-neighbour

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[26] T. Brennan and I. Bernal, *J. Phys. Chem.*, 1969, **73**, 443.

sulphur–sulphur distances in the cation range from 3.17 to 3.50 Å.

The remainder of the structure lacks the precision required for meaningful comparisons, owing to excessive thermal motion in the crystal. The BF_4^- ion in particular exhibits a high degree of librational shortening in some of the B–F bonds. There appear to be no significantly short intermolecular contacts (Table 2c).

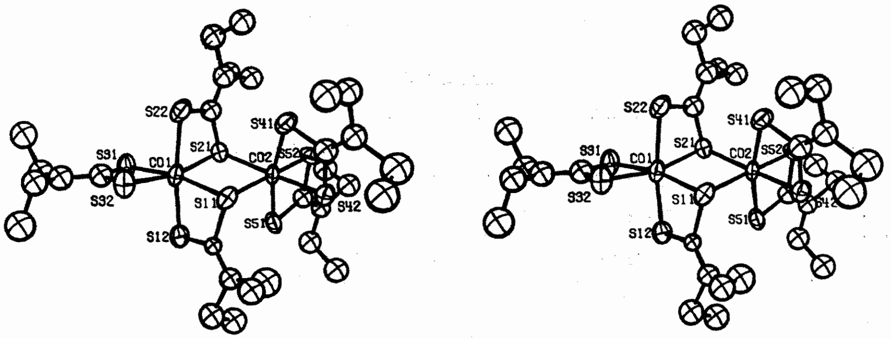

FIGURE 3 The $[Co_2(Et_2dtc)_5]^+$ cation; thermal ellipsoids enclose 20% probability

Recently the structure of a ruthenium dithiocarbamate cation, formed from the reaction of $[Ru(Et_2dtc)_3]$ and gaseous BF_3, has been reported.[27] As suspected [11] this complex is dimeric, $[Ru_2(Et_2dtc)_5]BF_4$. However, although the molecular formula type is identical with the cobalt(III) derivative, the molecular structure of the ruthenium(III) dimer differs significantly. The short Ru • • • Ru distance (2.74 Å) implies a metal–metal interaction which is absent in the cobalt analogue (Co • • • Co 3.37 Å). The ruthenium dimer has a non-chelating dithiocarbamate ligand which bridges the pair of ruthenium atoms (*cf.*, Figure 4) in the manner previously observed in the structure of $[Au(Pr^n{}_2dtc)]$.[28] In addition, the two dithiocarbamate ligands which function as bridging groups *via* their sulphur p_π electrons are chelated to different metal centres in the ruthenium dimer but to the same metal centre in the cobalt dimer. Unlike the cobalt complex, both ruthenium atoms possess the same chirality.

Recent work [2] on Mn^{IV} and Co^{IV} complexes of dithiocarbamates requires some comment. The properties of the Mn^{IV} salts of $[Mn(R_2dtc)_3]^+$ are in agreement with earlier results [4] and the crystal structure of the piperidyl derivative.[7] However, we have found the reactions of boron trifluoride etherate and gaseous boron trifluoride with $[Co(Et_2dtc)_3]$ and $[Co\{(C_6H_{11})_2dtc\}_3]$ always lead to the dimers $[Co_2(R_2dtc)_5]BF_4$. Surprisingly, the electronic spectral data reported for the suggested Co^{IV} species are virtually identical to that found here for $[Co_2(R_2dtc)_5]BF_4$ species. Although the published analytical and magnetic data [2] are not inconsistent with the Co^{IV} formulation, it would seem that the formulation as $[Co(R_2dtc)_3]^+$ must be regarded as being open to doubt.

The n.m.r. resonances of the cobalt dimers are not readily assigned. Coupling within the alkyl substituents and inequivalence of the ligands leads to complex spectra (Table 6). The simplest spectrum, that of $[Co_2(Me_2dtc)_5]BF_4$, shows five inequivalent CH_3 groups of equal intensity (Figure 5). Using the 'shift reagent' $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate), all peaks are moved downfield to different extents without showing evidence of further splitting. As the concentration of $[Eu(fod)_3]$ is increased, a peak due to $[Co(Me_2dtc)_3]$ grows progressively. The non-linear relationship between the concentration of $Eu(fod)_3$ and the shift of the five methyl peaks suggests this reagent is breaking up the dimer. $Eu(fod)_3$ does not induce shifts in the spectrum of $[Co(Me_2dtc)_3]$. The five lines observed in the spectrum of $[Co_2(Me_2dtc)_5]^+$ presumably arise from the diastereotopic nature of the protons on four of the ligands due to restricted rotation about the C$\overset{...}{-}$N bonds. The molecular symmetry of

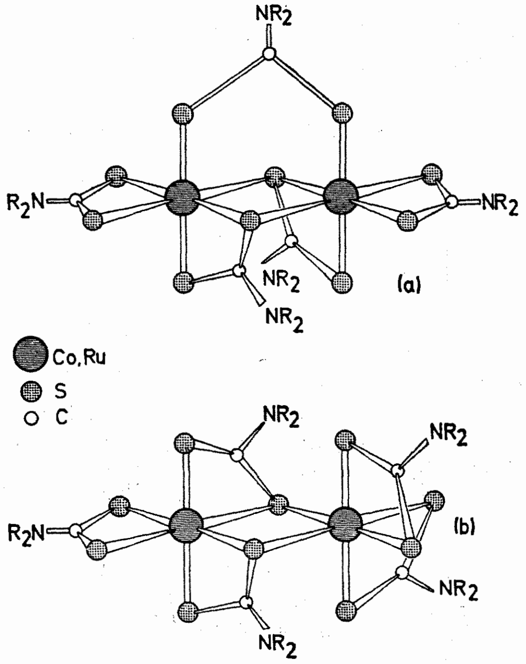

FIGURE 4 The structures of (a) the $[Ru_2(Et_2dtc)_5]^+$ and (b) $[Co_2(Et_2dtc)_5]^+$ cations

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[27] L. H. Pignolet and B. M. Mattson, *J.C.S. Chem. Comm.*, 1975, 49.

[28] R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.

the dimer (C_2) is the same as that in $[Co(Me_2dtc)_2(sacsac)]$ where the resonances of the diastereotopic methyl groups have been coalesced at 83 °C (*vide infra*).

The $-CH_2-$ resonance of $[Co\{(PhCH_2)_2dtc\}_3]$ is an *AB* quartet and is virtually unaffected by $Eu(fod)_3$ in $CDCl_3$. In $[Co_2\{(PhCH_2)_2dtc\}_5]BF_4$, fifteen lines are readily discernable (Figure 6) of an expected twenty lines assuming the complex exhibits a similar diastereoisomerism to that observed with $[Co_2(Me_2dtc)_5]^+$. $Eu(fod)_3$ has little effect on these resonances.

TABLE 6

N.m.r. spectra of cobalt(III) complexes

Compound	Chemical shift, δ/p.p.m.	Solvent
$[Co_2(Me_2dtc)_5]BF_4$	$-CH_3$ (3.20, 3.22, 3.31, 3.41, 3.57)	$CDCl_3$
$[Co_2(Me_2dtc)_5]BF_4$	$-CH_3$ (3.21 and others *)	CD_3CN
$[Co_2(Me_2dtc)_5]BF_4$	$-CH_3$ (3.23, 3.26, 3.36, 3.45, 3.60)	acetone-d_6
$[Co_2(Me_2dtc)_5]BF_4$	$-CH_3$ (3.18 and others *)	DMSO-d_6
$[Co_2(Me_2dtc)_5]BF_4$	$-CH_3$ (3.17, 3.18, 3.28, 3.38, 3.52)	CD_2Cl_2
$[Co_2\{(PhCH_2)_2dtc\}_5]BF_4$	$-CH_2-$ (4.2—5.7) aromatic (6.9—7.6) *	$CDCl_3$
$[Co_2(pyrrdtc)_5]BF_4$	$-CH_2-$ (2.1, 3.7) *	$CDCl_3$
$[Co_2(Et_2dtc)_5]BF_4$	$-CH_2-$ (3.8) * $-CH_3$ (1.4) *	$CDCl_3$
$[Co_2(MeBu^ndtc)_5]BF_4$	NCH_3 (3.14, 3.20, 3.24, 3.36, 3.49) Bu^n (3.6, 1.5, 1.0) *	$CDCl_3$
$[Co_2\{(C_6H_{11})_2dtc\}_5]BF_4$	CH (4.0) * $-CH_2-$ (1.3, 1.8) *	$CDCl_3$
$[Co_2(MeBu^ndtc)_5]BPh_4$	NCH_3 (3.06, 3.19, 3.20) * Bu^n (3.6, 1.5, 1.0) * BPh_4^-(6.8—7.5) *	$CDCl_3$
$[Co(Me_2dtc)_2(Pr^nOCS_2)]$	NCH_3 (3.26s) OCH_2 (4.50t) CH_2 (1.86 sextet) CH_3 (1.50t)	$CDCl_3$
$[Co(Me_2dtc)_2\{(C_6H_{11})_2dtc\}]$	NCH_3 (3.18s) cyclohexyl (1.28, 1.78, 2.14, 4.19) * C_5H_5 (7.32)	CD_2Cl_2
$[Co(Me_2dtc)_2\{(PhCH_2)_2dtc\}]$	NCH_3 (3.28, 3.26) $-CH_2-$ (4.82 AB quartet) C_5H_5 (7.31s)	$CDCl_3$
$[Co(Me_2dtc)_2(acac)]$	NCH_3 (3.30, 3.22) CH_3 (1.96) H (5.42)	CD_2Cl_2
$[Co(Me_2dtc)_2(sacsac)]$ †	NCH_3 (3.06, 3.03) CH_3 (2.20) H (2.71)	$NO_2C_6D_5$

* Resonances broad or multiplets. † OSi_2Me_6 as reference, otherwise tetramethylsilane.

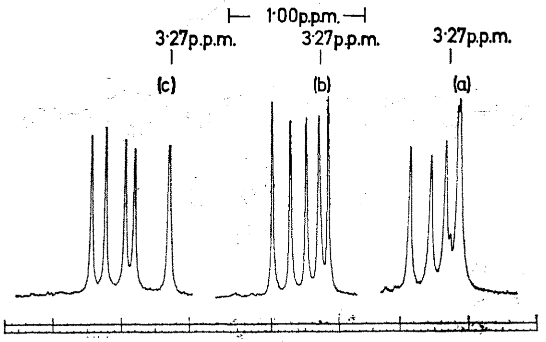

FIGURE 5 N.m.r. spectra of $[Co_2(Me_2dtc)_5]BF_4$ in $CDCl_3$; a, no added $Eu(fod)_3$, b and c, successive additions of $Eu(fod)_3$. The small peak at 3.27 p.p.m. is from $[Co(Me_2dtc)_3]$ impurity

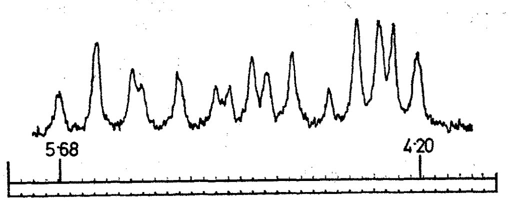

FIGURE 6 N.m.r. spectrum ($-CH_2-$) of $[Co_2\{(PhCH_2)_2dtc\}_5]BF_4$ in $CDCl_3$

These observations and the relatively long Co–S bond lengths joining the $Co(dtc)_3Co(dtc)_2^+$ units (*vide supra*) suggest the dimer is relatively unstable at the join of the two Co^{III} units and should react quite smoothly with selected co-ordinating ligands, *viz.*, acetylacetonate, dithioacetylacetonate, dithiocarbonates, and dithiocarbamates according to the general reaction scheme (1).

$$[Co_2(R_2dtc)_5]^+ + chel^- \longrightarrow [Co(R_2dtc)_3] + [Co(R_2dtc)_2(chel)] \quad (1)$$

The resulting mixed-ligand complexes of Co^{III} are relatively inert and may be separated from the other products, $[Co(Me_2dtc)_3]$ and $NaBF_4$ or KBF_4, by careful chromatography. Analytical and n.m.r. data (Tables 3 and 5) confirm the composition of the new mixed-ligand species. The reaction of the bidentate ligand with the dimer is quite clean and confirms that the complex is a ready source of a relatively reactive cobalt(III) unit, *viz.*, $[Co(R_2dtc)_2]^+$.

The n.m.r. inequivalence of the Me group on the dimethyldithiocarbamate ligands as observed in the cases where the extra chelate is $[acac]^-$, $[sacsac]^-$ or $[(PhCH_2)_2dtc]^-$ arises from the diastereotopic nature of Me groups in these complexes. A temperature-dependent n.m.r. study of these signals for $[Co(Me_2dtc)_2(sacsac)]$ in $NO_2C_6D_5$ reveals the signals coalesce to a broad peak at *ca.* 83 °C with the resulting peak becoming sharper up to 119 °C. At the latter temperature decomposition, presumably by ligand exchange, becomes important.

The dimer is apparently not stable in co-ordinating solvents. N.m.r. spectra of $[Co_2(Me_2dtc)_5]BF_4$ in CD_2Cl_2, deuterioacetone, and $CDCl_3$ show five inequivalent $-CH_3$ resonances. However, in deuterio-dimethyl sulphoxide and -acetonitrile one strong $-CH_3$ singlet is observed together with sundry small broad peaks in the same chemical shift region suggesting decomposition of the dimer to $[Co(Me_2dtc)_3]$ and other, presumably solvated, species.

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