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Dynamic Stereochemistry of Tris-Chelate Complexes. IV. Crystal Structure of Tris(*N*,*N*-diethyldithiocarbamato)ruthenium(III)[1]

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The crystal structure of tris(*N*,*N*-diethyldithiocarbamato)ruthenium(III), Ru(EtEt(dtc))$_3$, has been determined from three-dimensional counter data to assess the influence of solid-state structural parameters on the stereochemically nonrigid nature of Ru(dtc)$_3$ complexes in solution. The space group is $P2_1/c$ with lattice constants $a = 14.218$ (2) Å, $b = 10.432$ (2) Å, $c = 17.925$ (3) Å, $\beta = 116.86$ (1)°, and $Z = 4$. The data were refined by least-squares to a conventional R of 0.063. The average Ru–S distance is 2.38 Å and all six Ru–S distances are within 2σ of the average. The geometry of the RuS$_6$ core is typical of other M(dtc)$_3$ complexes in that a geometry intermediate between trigonal antiprismatic, TAP, and trigonal prismatic, TP, is found with approximate D_3 symmetry. The structural parameters are very similar to the ones of high-spin Fe(EtEt(dtc))$_3$ at 297°K but different from the 79°K parameters where the iron is low spin. The so-called average twist angle, ϕ, and the average propeller pitch angle, ψ, are 38 and 28°, respectively. The values for octahedral and TP geometry are $\phi = 60$ and 0° and $\psi = 35$ and 0°, respectively. The stereochemically nonrigid nature of Ru(dtc)$_3$ complexes which rearrange by the "trigonal-twist" mechanism can indeed be understood in terms of the ground-state geometry but this relation must be viewed with caution.

Introduction

The crystal structure of tris(*N*,*N*-diethyldithiocarbamato)ruthenium(III), Ru(EtEt(dtc))$_3$,[2] was determined in order to assess the influence of solid-state geometry on the stereochemically nonrigid nature of Ru(dtc)$_3$ complexes.[1] The paper immediately preceding this one (part III of the series) reports kinetic results for optical and geometrical isomerization of these complexes. The preceding paper should be read for a complete description of the kinetic results and for a rationale for this structure determination. In brief, Ru(dtc)$_3$ complexes represent the only class of ruthenium tris-chelate complex which is stereochemically nonrigid with respect to metal-centered inversion on the nmr time scale. For example, tris(tropolonato)[3] and -(β-diketonato)[4] complexes of Ru(III) are rigid at all accessible temperatures.[3,4] The mechanism of metal-centered inversion for the Ru(dtc)$_3$ complexes is proposed to be a trigonal twist which presumably requires a trigonal-prismatic transition state.[1] Structural studies which have been carried out on M(dtc)$_3$ complexes where M = Co,[5] Fe,[6,7] Mn,[8] and In[9] all show distortions toward trigonal-prismatic coordination geometry (*vide infra*). It is of interest to determine the distortion present in the case of ruthenium and to assess the generality of the contention[1,3,10,11] that a distortion toward trigonal-prismatic geometry influences the rate and mechanism for metal-centered inversion of tris-chelate metal complexes.

During the course of the kinetic investigation on the Ru(dtc)$_3$ complexes[1] it became clear that a detailed crystallographic investigation of a Ru(dtc)$_3$ complex would be needed. Although a communication[12] on the structure of Ru(EtEt(dtc))$_3$ appeared in 1966 which reported only the Ru–S bond lengths and the approximate average bite angle, we decided to resolve the structure because all attempts to obtain the crystallographic details from the authors[12] were unsuccessful.

Experimental Section

The preparation of the compound is described in the preceding paper.[1] Single crystals of Ru(EtEt(dtc))$_3$ were grown by slow evaporation from CH$_2$Cl$_2$–heptane solution. The crystal which was used for data collection was prismatic and had dimensions 0.28 × 0.40 × 0.48 mm^3, elongated parallel to c. The c axis was parallel to the spindle axis.

The systematic absences were obtained from Weissenberg film data (Cu Kα radiation) and are $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, which indicate the space group to be $P2_1/c$. This space group was used for solution and refinement of the structure. The unit cell dimensions are $a = 14.218$ (2) Å, $b = 10.432$ (2) Å, $c = 17.925$ (3) Å, and $\beta = 116.86$ (1)° and were determined by least-squares refinement using the θ angle values for eight Mo Kα peaks scanned with a diffractometer at room temperature. The measured density is 1.52 g/cm^3 from flotation which is in good agreement with the calculated value of 1.528 g/cm^3, with four molecules per unit cell. These values are in good agreement with the ones reported by Domenicano, *et al.*, for this compound.[12]

The reflections of the type $h + k = 2n + 1$ are very weak indicating that the lattice is pseudo-*C*-centered (*vide infra*). This phenomenon has been noticed by Leipoldt and Coppens[7] for Fe(EtEt(dtc))$_3$ which also has the room-temperature space group $P2_1/c$ with very similar unit cell dimensions.

Intensity data were collected at room temperature on a four-circle Hilger and Watts automatic diffractometer. The incident beam was Zr-filtered Mo Kα radiation. The scan was one-hundred 0.01° steps in θ and ω from −0.50 to +0.50° with respect to the calculated setting. The step time was 1 sec and the background was counted for 50 sec at each limit of the scan while crystal and counter were stationary. A total of 2786 independent reflections were collected over one quadrant for θ between 0 and 21°. Several low-angle reflections were omitted because extinction was suspected. The number of nonzero reflections (*i.e.*, with $F_o^2 > 2\sigma(F_o^2)$) used in the structure determination was 1698. Two standard reflection intensities were checked at intervals of 25 sequential reflections. No changes greater than 3% from the average value and no trend with time in the check reflections were noted.

The data were processed in the manner described by Corfield, Doedens, and Ibers;[13] the value of 0.03 was used for p in the $\sigma(I)$ equation. The intensity data were corrected for Lorentz and polari-

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[1] Part III: D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 13, 2045 (1974). The other papers in this series are listed in ref 1 of part III.

[2] Abbreviations used throughout for N substituents: Me = methyl, Et = ethyl, Bz = benzyl, Ph = phenyl, Pyr = pyrrolidyl or (CH$_2$)$_4$, Bu = *n*-butyl.

[3] S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 95, 1116 (1973), and references cited therein.

[4] J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, 5, 381 (1971).

[5] S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968).

[6] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972), and references cited therein.

[7] J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, 12, 2269 (1973).

[8] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972).

[9] P. J. Hauser, J. Bordner, and A. F. Schreiner, *Inorg. Chem.*, 12, 1347 (1973).

[10] S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972).

[11] D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

[12] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).

[13] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

zation effects and for absorption ($\mu = 7.57$ cm^{-1}) using the program DATAP2.[14] A grid size of 4 × 4 × 4 was used for the absorption correction.

The ruthenium and sulfur atoms were located from a three-dimensional Patterson map.[15] The subsequent three-dimensional Fourier map, phased by the ruthenium and sulfur atoms, showed most of the carbon and nitrogen atoms; however, C_2 symmetry appeared to be forced on the molecular structure presumably by the pseudo-*C*-centering. This model did not refine correctly after three cycles of full-matrix least-squares refinement with isotropic thermal parameters for all atoms. A similar problem was encountered for Fe(EtEt(dtc))$_3$.[7] A better model was found by using the crystallographic coordinates of the appropriate atoms (*i.e.*, Fe(S$_2$CNC$_2$)$_3$) of Fe(Pyr(dtc))$_3$[6] corrected for the unit cell dimensions and Ru positions of Ru(EtEt(dtc))$_3$. The model with all 25 atoms subsequently refined after several isotropic least-squares and Fourier passes to R = 0.082 and r = 0.036.[16] At this point in the refinement carbon atom C(C4) had a large temperature factor. Three more cycles of full-matrix least-squares refinement with the ruthenium and six sulfur atoms thermally anisotropic did improve the fit (R = 0.063, r = 0.020) but did not reduce the large temperature factor for C(C4). This carbon atom position also yielded an unreasonable C(C2)–C(C4) bond length of *ca.* 1 Å. A three-dimensional difference Fourier map calculated from the positions of all atoms excluding C(C4) yielded a large region of spread-out electron density with no distinct maxima in the region of C(C4). Disorder was suspected; however, several attempts to solve the problem failed.[17] The final three cyles of full-matrix least-squares refinement with the ruthenium and six sulfur atoms thermally anisotropic was performed with C(C4) fixed at a chemically reasonable distance from C(C2) in the region of greatest electron density. The final agreement factors are R = 0.063, r = 0.024. Further refinement was not attempted for the following reasons: (i) all of the full shifts in the thermal and positional parameters for the 24 refined atoms in the last cycle of least-squares refinement were much less than the standard deviations; (ii) the chemically sought information, *i.e.*, the geometry of the RuS$_6$ core, is obtainable and not significantly affected by the disorder. Elemental analysis and pmr results show that the compound is pure and is indeed Ru(EtEt(dtc))$_3$ which eliminates the possibility of an impurity or an incorrectly formulated compound as a cause of the disorder. The numbers of observations and variables are respectively 1698 and 131 in the final refinements.

When pseudosymmetry is present (*vide supra*) such that the reflections divide into two sets, one set generally intense ($h + k = 2n$) and the second set generally weak ($h + k = 2n + 1$), there is the possibility of a false solution which satisfies the intense set of data but not the weak set. If due allowance is made for their generally smaller intensity, the $h + k = 2n + 1$ reflections fit the model as well as the $h + k = 2n$ reflections which verifies the correctness of the model.

The final atomic coordinates with their standard deviations and the final anisotropic and isotropic thermal parameters with their standard deviations are given in Table I. A table of observed and calculated structure factors is available.[18]

Results and Discussion

RuS$_6$ Core. The numbering system is shown in Figure 1 and the interatomic distances and angles are summarized in Table II.

Table I. Final Atomic Fractional Coordinates and Thermal Parameters with Standard Deviations

Atom	x	y	z	B, Å^2
Ru	0.2516 (1)[a]	0.2479 (1)	0.2515 (1)	b
S(A1)	0.1636 (3)	0.0539 (4)	0.2506 (3)	b
S(A2)	0.3658 (3)	0.0767 (4)	0.2585 (3)	b
S(B1)	0.1609 (3)	0.2749 (4)	0.1040 (3)	b
S(B2)	0.3436 (3)	0.4083 (4)	0.2157 (3)	b
S(C1)	0.1370 (3)	0.3805 (4)	0.2805 (3)	b
S(C2)	0.3394 (3)	0.2951 (4)	0.3968 (3)	b
C(A1)	0.2704 (10)	−0.0281 (13)	0.2534 (9)	3.9 (3)
N(A)	0.2776 (9)	−0.1496 (12)	0.2541 (8)	4.8 (3)
C(A2)	0.1934 (15)	−0.2395 (18)	0.2526 (12)	7.1 (4)
C(A3)	0.3722 (14)	−0.2164 (16)	0.2556 (11)	6.0 (4)
C(A4)	0.1270 (19)	−0.2786 (22)	0.1620 (15)	10.1 (7)
C(A5)	0.4509 (17)	−0.2600 (20)	0.3452 (14)	8.8 (5)
C(B1)	0.2544 (9)	0.3884 (13)	0.1130 (8)	3.2 (3)
N(B)	0.2579 (8)	0.4470 (11)	0.0493 (7)	3.9 (2)
C(B2)	0.1728 (12)	0.4269 (15)	−0.0370 (10)	5.3 (4)
C(B3)	0.3317 (12)	0.5583 (15)	0.0648 (10)	5.1 (3)
C(B4)	0.0909 (15)	0.5333 (19)	−0.0658 (12)	8.1 (5)
C(B5)	0.3778 (14)	0.5578 (18)	0.0035 (11)	7.2 (4)
C(C1)	0.2316 (9)	0.3853 (13)	0.3823 (9)	3.3 (3)
N(C)	0.2239 (9)	0.4441 (12)	0.4434 (8)	4.9 (3)
C(C2)	0.1162 (19)	0.5110 (24)	0.4324 (16)	11.5 (7)
C(C3)	0.3094 (11)	0.4511 (15)	0.5299 (9)	4.7 (3)
C(C4)	0.1293[c]	0.6477[c]	0.4293[c]	18.0[c]
C(C5)	0.3848 (14)	0.5512 (19)	0.5464 (12)	7.7 (5)

Atom	$10^4\beta_{11}$[d]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru	54 (1)	76 (1)	34 (1)	3 (1)	2 (0.5)	2 (1)
S(A1)	66 (3)	89 (4)	45 (2)	−5 (3)	24 (2)	3 (3)
S(A2)	70 (3)	70 (4)	43 (2)	1 (3)	23 (2)	0 (2)
S(B1)	58 (3)	90 (5)	34 (2)	−10 (3)	15 (2)	−4 (2)
S(B2)	68 (3)	109 (5)	33 (2)	−22 (3)	11 (2)	−3 (3)
S(C1)	62 (3)	145 (6)	35 (2)	26 (3)	12 (2)	−3 (3)
S(C2)	58 (3)	104 (5)	35 (2)	13 (3)	12 (2)	0 (3)

[a] The numbers in parentheses in this and succeeding tables represent the estimated standard deviation of the last significant figure(s). [b] Atoms refined anisotropically. [c] Coordinates and thermal parameter not refined in last refinement (see Experimental Section). [d] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)]$.

Table II. Interatomic Distances and Angles within the RuS$_6$ Polyhedron[a]

Distances, Å

Ru–S(A1)	2.376 (4)	S(C1)–S(C2)	2.829 (5)
Ru–S(A2)	2.378 (4)	S(A1)–S(B1)	3.483 (5)
Ru–S(B1)	2.377 (4)	S(A1)–S(C1)	3.495 (5)
Ru–S(B2)	2.383 (4)	S(B1)–S(C1)	3.507 (5)
Ru–S(C1)	2.368 (4)	S(A2)–S(B2)	3.526 (5)
Ru–S(C2)	2.376 (4)	S(A2)–S(C2)	3.509 (5)
S(A1)–S(A2)	2.825 (5)	S(B2)–S(C2)	3.479 (5)
S(B1)–S(B2)	2.827 (5)		

Angles, Deg

S(A1)–Ru–S(A2)	72.9 (1)	S(B2)–Ru–S(C2)	94.0 (1)
S(B1)–Ru–S(B2)	72.9 (1)	S(A1)–Ru–S(C2)	101.4 (1)
S(C1)–Ru–S(C2)	73.2 (1)	S(B1)–Ru–S(A2)	99.4 (1)
S(A1)–Ru–S(B1)	94.2 (1)	S(C1)–Ru–S(B2)	99.5 (1)
S(A1)–Ru–S(C1)	94.9 (1)	S(A1)–Ru–S(B2)	161.4 (2)
S(A2)–Ru–S(B2)	95.6 (1)	S(B1)–Ru–S(C2)	161.2 (1)
S(A2)–Ru–S(C2)	95.2 (1)	S(C1–Ru–S(A2)	161.5 (2)
S(B1)–Ru–S(C1)	95.3 (1)		

[a] For numbering system see Figure 1.

The mean Ru–S distance is 2.376 Å with all six Ru–S distances within 2σ or ~0.008 Å of the mean. Significant differences (up to 0.05 Å) in M–S distances have been noted for low-spin d^5 iron(III) complexes containing the MS$_6$ core. In the low-spin complex tris(*O*-ethyldithiocarbonato)iron(III)[19] and in the predominantly low-spin complex Fe(MePh(dtc))$_3$[6] a distortion, which is characterized by three short and three long Fe–S distances such that the long and short

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(14) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, 18, 1035 (1965).

(15) Three local programs by Dr. L. W. Finger were used to solve and refine the structure: UMPREL for statistics and Patterson map; UMLSTSQ for full-matrix least-squares refinement; and BADTEA for bond distances, angles, and errors. All data processing was done with the Control Data 6600 computer at the University of Minnesota Computer Center.

(16) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$; the numerator or r was the function minimized; the weights were $1/[\sigma(F^2)]^2$ where $\sigma(F_o^2) = \sigma(I)/Lp$. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A (S, C, N) and Table 3.3.1B (Ru). Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for ruthenium: $\Delta f' = -1.2$, $\Delta f'' = 1.1$.

(17) Leipoldt and Coppens[7] noted a similar disorder in the structure of Fe(EtEt(dtc))$_3$ at 297°K. They also found the same shortened C–C bond length (Table VIII of ref 7).

(18) See paragraph at end of paper regarding supplementary material.

(19) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970).

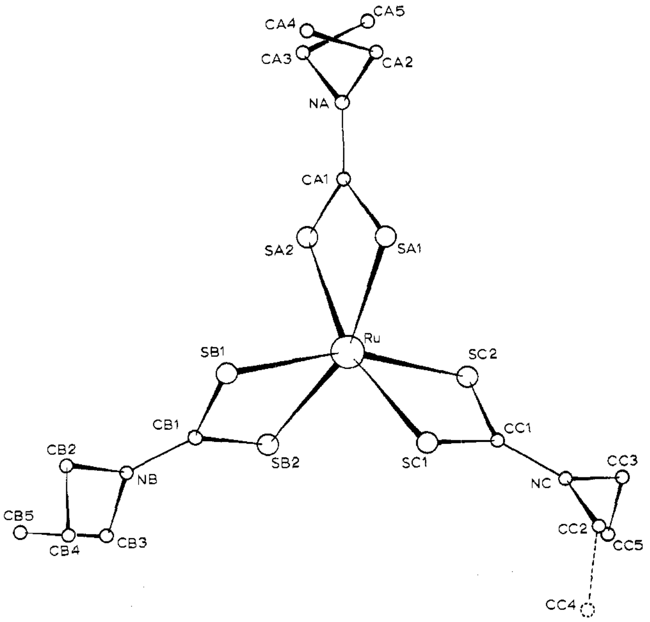


Figure 1. Drawing of the Ru(EtEt(dtc))$_3$ molecule viewed along the $\sim C_3$ symmetry axis showing the labeling scheme. Carbon atom CC4 was not refined (see text).

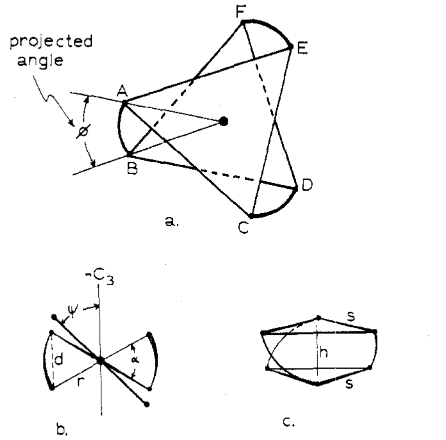


Figure 2. Various views of the coordination core of a tris-chelate complex which define the twist angle ϕ, pitch angle ψ, bite angle α, bite distance d, metal-ligand distance r, polyhedron side s, and polyhedron height h. In Part b all the angles shown are real angles, *i.e.*, not projections. For example, ψ is the angle between the plane of the chelate ring and the C_3 axis.

distances belong to opposite parallel triangles of sulfur atoms (triangles ACE and BDF in Figure 2a), has been observed and attributed[6] to Jahn-Teller and spin-orbit interactions. No such distortion is observed in high-spin iron(III) complexes.[6,7] If the explanation for this phenomenon is correct, the ruthenium(III) complex, which is low spin and will have greater spin-orbit interaction, should show an enhanced distortion. The fact that this distortion is not present indicates that the above explanation is probably incorrect. The low-spin complex Fe(EtEt(dtc))$_3$ at 79°K also does not show any significant differences in Fe-S distances.[7]

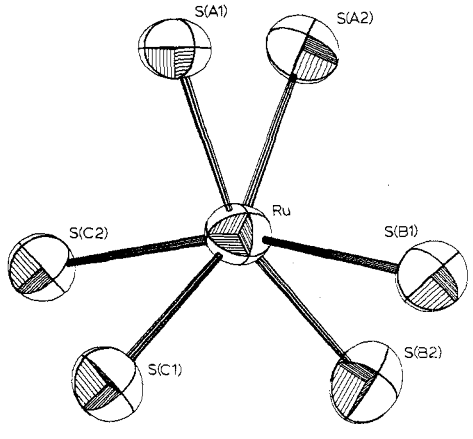


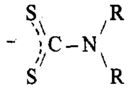
Figure 3. ORTEP drawing of the RuS$_6$ core showing the anisotropic thermal ellipsoids. Ellipsoids are 50% probability surfaces.

Structural parameters for some complexes containing the MS$_6$ core are summarized in Table III and defined in Figure 2. These parameters completely characterize the MS$_6$ polyhedron. A complete discussion including the complexes in this table other than the ruthenium complex appears in a later section. The RuS$_6$ polyhedron has approximate D_3 symmetry. The two S$_3$ triangles (ACE and BDF in Figure 2a) are very nearly parallel with an angle between the planes of the triangles of *ca.* 2°. This is a general characteristic of M(dtc)$_3$ complexes.[20,21] The geometry of Ru(EtEt(dtc))$_3$ is best described by comparing it to octahedral (O_h) and trigonal-prismatic (TP) geometries. Angular structural parameters for these limiting cases are given in Table III. O_h geometry requires a bite angle, α, of 90° so Ru(EtEt(dtc))$_3$ cannot be O_h because the average value of α is 73.0°. The molecule therefore is "twisted" toward TP geometry and maintains $\sim D_3$ symmetry. This is reflected by the twist angle ϕ and the propeller pitch angle ψ (defined in Figure 2) both of which have values between those expected for O_h and TP geometry. The RuS$_6$ polyhedron is flattened, however, as indicated by a side to height ratio, s/h, of 1.40. Known complexes of TP geometry have s/h values of *ca.* 1;[22,23] however, this is not required by TP geometry.

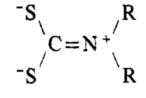
The best parameter to characterize the amount of twist from O_h or TP geometry is the pitch angle ψ (providing *ca.* D_3 symmetry is maintained). For example, a value of $\alpha <$ 90° requires some change away from O_h geometry; however, the entire change could result in a greatly decreased ϕ with ψ remaining at the O_h value of 35.3°. If this occurred, in the limit of very small values for α, a triangle would be approached. The fact that ψ also changes, *i.e.*, the propeller pitch changes toward the TP value of 0°, means a twist toward TP geometry has occurred in this and indeed most M(dtc)$_3$ complexes.

An ORTEP drawing of the RuS$_6$ core viewed along the $\sim C_3$ symmetry axis is shown in Figure 3. The anisotropic thermal ellipsoids show no abnormal motion.

Geometry of the Ligands. The numbering system is shown in Figure 1 and the ligand interatomic distances and angles are summarized in Table IV. The distances and angles are similar to those found in other dithiocarbamato complexes. Resonance structure Ib makes an important



Ia



Ib

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[20] Exceptions to this have been noted in the cases of Mn(EtEt(dtc))$_3$[8] and As(EtEt(dtc))$_3$.[21] The former possesses a tetragonal distortion (*vide supra*) while the latter has partial metal-ligand ionic bonding and approaches coordination number 3. In(Pyr(dtc))$_3$[9] also shows a significant deviation from D_3 symmetry.

[21] M. Colapietro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Commun.*, 302 (1968).

[22] E. I. Steifel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972), and references cited therein.

[23] M. R. Churchill and A. H. Reis, Jr., *Inorg. Chem.*, 12, 2280 (1973), and references cited therein.

Table III. Crystallographic Parameters[a] of the MS_6 Core for M(dtc)$_3$ Complexes which Possess ~D_3 Symmetry

Complex[b]	r, Å	d, Å	s, Å	h, Å	α, deg	ϕ,[c] deg	ψ, deg	s/h	Ref
Ru(EtEt(dtc))$_3$	2.38	2.83	3.50	2.50	73.0	38.1	27.8	1.40	This work
Fe(EtEt(dtc))$_3$	2.36	2.84	3.44	2.54	74.3	37.6	26.7	1.35	*e*
Fe(EtEt(dtc))$_3$ (79°K)	2.31	2.84	3.36	2.50	75.9	40.4	28.2	1.34	*e*
Fe(Pyr(dtc))$_3$	2.41	2.91	3.50	2.60	74.4	37.4	26.5	1.35	*f*
Fe(MePh(dtc))$_3$	2.31	2.82	3.38	2.47	75.1	40.7	28.9	1.37	*f*
Co(EtEt(dtc))$_3$	2.26	2.79	3.32	2.39	76.2	43.7	30.7	1.39	*g*
In(Pyr(dtc))$_3$	2.59	2.95	3.84	2.66	69.4	32.8[d]	25.3	1.44	*h*
Ni(BuBu(dtc))$_3^+$	2.26	2.79	3.34	2.37	76.3	45.3	32.1	1.41	*i*
O_h					90	60	35.3	1.22	
TP (D_{3h})						0	0	~1[j]	

[a] Parameters are defined in Figure 2 and text; average values are listed and were calculated from the crystallographic coordinates given in the appropriate reference. [b] All structures were determined at room temperature unless stated otherwise; abbreviations are listed in ref 2. [c] Values differ slightly from those reported elsewhere due to the method of calculation; however, these values are correct for relative comparison. [d] This value differs significantly from the reported value which is in error. [e] Reference 7. [f] Reference 6. [g] Reference 5. [h] Reference 9. [i] J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Amer. Chem. Soc.*, **95**, 774 (1973). [j] This value is usually found for TP complexes, for example, in the TP tris(dithiolenes); however, it is not required by D_{3h} geometry.

Table IV. Interatomic Distances and Angles within the Ligands[a]

	Ligand A	Ligand B	Ligand C
	Distances, Å		
S(1)-C(1)	1.72 (1)	1.73 (1)	1.71 (1)
S(2)-C(1)	1.71 (1)	1.71 (1)	1.72 (1)
C(1)-N	1.27 (2)	1.32 (2)	1.30 (2)
N-C(2)	1.51 (2)	1.49 (2)	1.61 (3)[b]
N-C(3)	1.51 (3)	1.50 (2)	1.48 (2)
C(2)-C(4)	1.52 (3)	1.52 (3)	1.44 (3)[b]
C(3)-C(5)	1.55 (3)	1.51 (3)	1.43 (3)[b]
	Angles, Deg		
Ru-S(1)-C(1)	88.1 (5)	88.3 (5)	87.9 (5)
Ru-S(2)-C(1)	88.3 (5)	88.5 (5)	87.5 (5)
S(1)-C(1)-S(2)	110.6 (8)	110.3 (8)	111.3 (9)
S(1)-C(1)-N	124.1 (12)	124.5 (8)	125.9 (10)
S(2)-C(1)-N	125.3 (12)	125.2 (9)	122.7 (9)
C(2)-N-C(3)	114.0 (13)	118.2 (12)	113.1 (14)
N-C(2)-C(4)	106.9 (17)	112.9 (14)	107.4 (18)[b]
N-C(3)-C(5)	112.0 (18)	111.0 (14)	116.0 (14)

[a] For numbering system see Figure 1. [b] This distance or angle involves a disordered carbon atom (see text).

contribution to the bonding of the dithiocarbamate ligand in all M(dtc)$_3$ complexes. This is demonstrated by short nearly double-bond S_2C-N distances and long nearly single-bond S-C distances. The average S_2C-N and S-C distances in the ruthenium complex are 1.30 (2) and 1.72 (1) Å, respectively, which are respectively among the shortest and longest values yet observed. The corresponding average values in other M(EtEt(dtc))$_3$ complexes are 1.34 (1) and 1.71 (1) (M = Fe, 297°K),[7] 1.323 (6) and 1.721 (4) (M = Fe, 79°K),[7] 1.31 (1) and 1.71 (1) (M = Co),[5] and 1.35 (3) and 1.65-1.77 (2) Å (M = Mn).[8] These distances are all very similar; however, the ruthenium complex appears to have a slightly greater amount of resonance structure Ib which is consistent with its higher barrier to S_2C-N bond rotation which has been measured by nmr line-broadening techniques for the analogous M(MePh(dtc))$_3$ complexes. These barriers for manganese,[24] iron,[25] and ruthenium,[1] are respectively 11.8, 12.0, and 15.6 kcal/mol.

One of the ethyl groups of ligand C is apparently disordered (see Experimental Section). C(C4) and C(C2) have large isotropic thermal parameters and are the atoms primarily affected by disorder; therefore, the distances and angles involving these atoms are not meaningful. It is not obvious what causes the disorder nor how to correct for it; however, the exact same problem was noted in the room-temperature structure of Fe(EtEt(dtc))$_3$.[7] This compound crystallizes in the same space group with almost identical unit cell dimensions: $P2_1/c$, a = 14.29 (1) Å, b = 10.37 (1) Å, c = 17.87 (1) Å, and β = 116.6 (1)° compared with a = 14.22 (0.2) Å, b = 10.43 (0.2) Å, c = 17.93 (0.3) Å, and β = 116.8 (0.1)° for the ruthenium complex. In fact the two structures have almost identical atomic coordinates with an average difference of about 4σ. The disorder shows up in the same ethyl group in both structures.[26]

Intermolecular Distances. There are no abnormally close intermolecular contacts. The closest approach of a sulfur atom of one molecule with any atom of another is 3.76 Å for S(A1)-C(CB2)′ where the prime denotes a different molecule. The closest intermolecular S-S′ distance is 4.32 Å for S(A2)-S(B2)′ and the closest C-C intermolecular distance omitting ones involving disordered C(C4) is 3.79 Å for C(C5)-C(A5)′.

Discussion of the MS_6 Core in Relation to Other M(dtc)$_3$ Complexes. Table III lists the relevant structural parameters which are defined in Figure 2 for all M(dtc)$_3$ complexes for which complete structures have been reported and for which ~D_3 symmetry has been found. In(Pyr(dtc))$_3$ is significantly distorted from D_3 symmetry but is included because it represents the only complex (other than the present work) of a fifth-row element. The striking similarity of the ruthenium parameters with those of Fe(EtEt(dtc))$_3$ and Fe(Pyr(dtc))$_3$ should be evident. These iron complexes are predominantly high spin with solid-state room-temperature μ_{eff} values of 4.3 and 5.9 BM, respectively, whereas the ruthenium complex is low spin (μ_{eff} = 1.86 BM). The predominantly low-spin complexes of iron(III), Fe(EtEt(dtc))$_3$ (79°K, μ_{eff} = 2.2 BM) and Fe(MePh(dtc))$_3$ (μ_{eff} = 2.9 BM), have parameters which are different; namely, r and s increase and α, ϕ, and ψ decrease on going from low-spin to high-spin iron(III). The expansion of the coordination core and the increased twisting toward TP geometry for high-spin Fe(III) compared to low-spin Fe(III) has been discussed by others[6,7] and is well known. It is perhaps surprising that the Ru(III) complex is so similar to high-spin Fe(III); however, the similar metal-sulfur bond length is to be expected and clearly plays a role in determining the relative twist toward TP geometry. For example, the In(III) complex has the longest M-S distance and is the most twisted toward TP geometry whereas the

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(24) B. L. Edgar, L. Que, Jr., and L. H. Pignolet, in preparation.

(25) B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Amer. Chem. Soc.*, **95**, 1125 (1973); Fe(MePh(dtc))$_3$ has a spin state equilibrium and is predominantly low spin.

(26) Leipoldt and Coppens[7] reported the atomic coordinates for a different molecule in the unit cell. To convert their coordinates into ours add $^1/_2$ to all x positions; for C(4) and C(5) in ligand 2 apply $^1/_2 - y$ and $z - {}^1/_2$ transformations; and for C(2) and C(3) in ligand 3 apply $^1/_2 - y$ and $^1/_2 + z$. Note that there is a labeling error in ref 7: atoms C(2) and C(3) in ligand 3 should be labeled C(4) and C(5) and *vice versa*.

Co(III) and Ni(IV) complexes have the shortest M–S distances and the largest ϕ and ψ values.

Large M–S distances correspond to the smaller bite angles, α. If $\alpha < 90°$, the complex cannot have O_h geometry and therefore must be distorted away from this geometry in some way (*vide supra*). Most of the M(dtc)$_3$ complexes choose to distort toward TP coordination; *i.e.*, they maintain $\sim D_3$ symmetry while both ϕ and ψ decrease. The smaller α becomes, the closer the geometry approaches the TP limit; however, none of these compounds are distorted anywhere near 50% from O_h toward TP. Indeed, the smallest propeller pitch angle, ψ, is *ca.* 25° which is a long way from 0°.

All of the M(dtc)$_3$ complexes are compressed relative to the octahedron ($s/h > 1.22$) or the experimentally found trigonal prism ($s/h \simeq 1$). No trend in s/h exists for these complexes. The most compressed is In(Pyr(dtc))$_3$ (smallest α of 69.4°) while the next most compressed is Ni(BuBu(dtc))$_3^+$ (largest α of 76.3°).

Relation of Structure to Rate of Metal-Centered Inversion. Ru(dtc)$_3$ complexes represent the only tris-chelate compounds of ruthenium(III) which are stereochemically nonrigid with respect to metal-centered rearrangement on the nmr time scale.[1,27] The structural parameters for Ru(EtEt(dtc))$_3$ indicate a geometry intermediate between trigonal antiprismatic ($\phi = 60°$), TAP, and TP. The mechanism for metal-centered rearrangement of Ru(dtc)$_3$ complexes has been shown to involve the trigonal-twist pathway.[1] This mechanism has a TP transition state and presumably can occur with greater ease if the ground-state geometry is intermediate between TAP and TP geometry. Structures have not been determined for other tris-chelate complexes of Ru(III) but structural results of similar compounds suggest that tris(β-diketonate) and tris(tropolonate) complexes are $\sim O_h$.[28-30] This may explain why these complexes are rigid with respect to metal-centered rearrangement, at least *via* a trigonal-twist pathway. All evidence to date suggests that the various bond rupture mechanisms which have been established for several tris(β-diketonates)[31,32] give higher activation energies than the trigonal-twist pathway.[3] Therefore, complexes which have solid-state geometries intermediate between TAP and TP are usually stereochemically nonrigid and in all cases rearrange *via* the trigonal-twist mechanism. Some caution must be observed here, however, because it is not always true that for complexes which rearrange *via* the trigonal-twist mechanism the most twisted (toward TP) rearrange faster. For example, Co(α-C$_3$H$_5$T)$_3$[3] has a lower activation energy for optical inversion than Co(BzBz(dtc))$_3$[33] even though the dtc complex is much more twisted toward TP geometry. A more detailed discussion which relates ground-state structure to rate of metal-centered rearrangement is presented in the previous paper.[1]

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2051.

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(28) All tris(β-diketonate) complexes are $\sim O_h$ with the exception of that of Mn(III)[29] which shows a tetragonal distortion. Al(T)$_3$[30] is slightly distorted toward TP with $\phi = 48°$ and $\psi = 31°$ whereas Co(T)$_3$[10] has $\phi \approx 55°$. Note Added in Proof. The structure of Ru(acac)$_3$ has been carried out and $\sim O_h$ geometry is found ($\alpha = 93.7°$, $\phi = 64.4°$, $\psi = 36.2°$): G. K.-J. Chou, R. L. Sime, and R. J. Sime, *Acta Crystallogr., Sect. B*, **29**, 2845 (1973).

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