shell more efficiently for the smaller cations, as the 3250-cm^{-1} band, for the outer-shell H_2O molecules, becomes relatively more intense through the series Li^+, Na^+, and K^+. Also, the downshift in the non-H-bonded mode from 3590 cm^{-1} for $KClO_4$ to 3530 cm^{-1} for $LiClO_4$ suggests an enhanced ability of the H_2O, attached to the smaller cations, to interact with neighboring ClO_4^- ions.

Acknowledgment. This research has been sponsored by the National Science Foundation.

Registry No. H_2O, 7732-18-5; $LiClO_4$, 7791-03-9; $NaClO_4$, 7601-89-0; $KClO_4$, 7778-74-7; $NaClO_3$, 7775-09-9; $NaNO_3$, 7631-99-4.

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Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Synthesis and Characterization of a New Seven-Coordinate Ruthenium(IV) Complex. Crystal and Molecular Structure of Iodotris(*N*,*N*-dimethyldithiocarbamato)ruthenium(IV)–Iodine

B. M. Mattson and L. H. Pignolet*

Received September 20, 1976 AIC60690P

The reaction of iodine with various bis- and tris(*N*,*N*-disubstituted-dithiocarbamato)metal complexes, $M(R_2dtc)_n$, $n = 2$ or 3, has been shown to form stable complexes in which the metal is in an unusually high oxidation state. Included among these are $[Ni(Bu_2dtc)_3]I_n$, $n = 1$ or 3 (Bu = *n*-butyl),[1,2] $[M(Bu_2dtc)_3]I_3$, M = Pd or Pt,[3] $[Cu(Bu_2dtc)_2]$,[2,4] and *cis*-$Pt(Bu_2dtc)_2I_2$.[3] In all but the last example the iodine functions as a counteranion, I^- or I_3^-. *cis*-$Pt(Bu_2dtc)_2I_2$ has been characterized by x-ray analysis[3] and is synthesized initially in the trans stereochemistry by an interesting solid-state reaction between $Pt(Bu_2dtc)_2$ and I_2. The compound rapidly converts into the cis form in solution.[3]

In this note we report the reaction between iodine and $M(R_2dtc)_3$ complexes where M = iron and ruthenium in CH_2Cl_2 solution. A rapid reaction occurs with complexes of both metals yielding pure crystalline compounds. In the case of ruthenium a diamagnetic complex is formed with stoichiometry $Ru(R_2dtc)_3I_3$ for $R_2 = Me_2$, Et_2, Bzl_2, and (Me)(Ph) (Me = methyl, Et = ethyl, Bzl = benzyl, Ph = phenyl). An x-ray analysis for $R_2 = Me_2$ shows the molecule to be seven-coordinate and to have a distorted pentagonal-bipyramidal geometry with two R_2dtc ligands spanning equatorial sites and the third spanning axial and equatorial sites. One iodine atom is covalently coordinated to the ruthenium atom in an axial position while an I_2 molecule strongly solvates the iodine atom. The compound is structurally similar to three other d^4 metal complexes, $Ru(Et_2dtc)_3Cl$,[5] $Mo(Bu_2dtc)_3NO$,[6] and $Re(Et_2dtc)_3CO$.[7] The x-ray analysis was carried out in order to account for unusual ^1H NMR properties (vide infra) and to elucidate the nature of the iodine atoms and the geometry of the coordination core. The analogous reaction with the iron complex ($R_2 = Me_2$) yielded a paramagnetic compound which is identified to be $Fe(Me_2dtc)_2I$.[8] Details of the characterization of these complexes and the x-ray structure of $Ru(Me_2dtc)_3I{\cdot}I_2$ are reported in this note.

Experimental Section

Spectra. ^1H NMR spectra were recorded using a Varian XL-100-15 spectrometer equipped with a variable-temperature probe. IR spectra were recorded in KBr disks with a Perkin-Elmer Model 237 grating spectrophotometer. Electronic absorption spectra were obtained in CH_2Cl_2 solution at 25 °C with a Cary Model 14 spectrophotometer. Magnetic susceptibilities were determined by the Faraday method at 25 °C using $Hg[Co(SCN)_4]$ as calibrant.

Conductivity experiments were carried out using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Reagent grade nitromethane was purified by double distillation from anhydrous $CaCl_2$ onto anhydrous $CaSO_4$ under nitrogen and Spectrograde 1,2-dichloroethane was used without purification.

Preparation of Compounds. $Ru(R_2dtc)_3I_3$. $Ru(Me_2dtc)_3$, 0.5 g purified by column chromatography,[9] was dissolved in ca. 300 ml of CH_2Cl_2 and then filtered. I_2 (0.4 g) was dissolved in CH_2Cl_2 and added to the solution of $Ru(Me_2dtc)_3$ affording metallic gold crystals of $Ru(Me_2dtc)_3I_3$. Recrystallization was achieved by continuous Soxhlet extraction using CH_2Cl_2. Anal. Calcd for $RuC_9H_{18}N_3S_6I_3$: C, 12.83; H, 2.15. Found: C, 13.09; H, 2.21. Electronic absorption spectrum (λ_{max} (nm), log ϵ): 265, 4.59; 289, 4.60; 356, 4.34; 460 sh, 3.58. IR spectrum (cm^{-1}) (ν_{C-N} 1548, 1537): 1391, 1249, 1151. ^1H NMR (CD_2Cl_2): τ 6.91 (singlet). Mp 218 °C dec; conductivity (8.31×10^{-4} M in nitromethane at 25 °C) $\Lambda = 77\ \Omega^{-1}\ cm^2\ mol^{-1}$. Analogous complexes with $R_2 = Et_2$, Bzl_2, and (Me)(Ph) were prepared in an identical manner except that purification was achieved by recrystallization from CH_2Cl_2–heptane solution. Complete characterization data for these compounds are listed in supplementary Table SI.

$Fe(Me_2dtc)_2I$ was prepared in a manner identical manner with that for $Ru(R_2dtc)_3I_3$, and purification was achieved by Soxhlet extraction from CH_2Cl_2. Anal. Calcd for $FeC_6H_{12}N_2S_4I$: C, 17.03; H, 2.86; N, 6.62; I, 29.99. Found: C, 17.07; H, 2.91; N, 6.53; I, 30.19. Electronic absorption spectrum (λ_{max} (nm), log ϵ): 305, 4.29; 377, 4.10; 456, 3.93; 500 sh, 3.78; 604, 3.66. IR spectrum (cm^{-1}) ($\nu_{C\cdots N}$ 1550): 1391, 1239, 1151, 922. Mp 307 °C dec; magnetic susceptibility $\chi_m^{cor} = 700 \times 10^{-5}$ cgsu/mol at 25 °C; $\mu_{eff} = 4.09\ \mu_B$.

Structure Determination. The quality of the crystals was poor so that much difficulty was encountered in finding a suitable one. We proceeded with a small flat needle-shaped crystal of dimensions 0.28 mm × 0.12 mm × 0.04 mm. The monoclinic crystal was mounted with the *a* axis parallel to the spindle axis. The cell constants, $a = 6.261$ (6) Å, $b = 17.178$ (10) Å, $c = 10.986$ (7) Å, $\beta = 103.83$ (5)°, and $V = 1147$ Å^3, were determined by a least-squares refinement using θ-angle values for 10 Mo Kα peaks carefully centered on the diffractometer. The measured density, 2.40 g/cm^3, agrees with the calculated density, 2.44 g/cm^3, for $Z = 2$. Systematic extinctions, ($0k0$, $k \neq 2n$), indicated the space group to be $P2_1$ or $P2_1/m$. The latter was confirmed by the solution of the structure. Since $Z = 2$, this requires that individual molecules contain either a mirror plane or a center of symmetry.

Intensity data were collected on a four-circle Hilger and Watts automatic diffractometer using Zr-filtered Mo Kα radiation. Of the 1702 independent reflections collected out to $\theta = 26°$, 1257 with $F_o^2 > 2\sigma(F_o^2)$ were used in solution and refinement of the structure. Two standard reflection intensities were checked at intervals of 20 sequential reflections and no changes greater than 4% from the average value and no trends with time were noted.

The data were processed in the manner described by Corfield, Doedens, and Ibers,[10] using 0.03 for *p* in the $\sigma(I)$ equation. The intensity data were corrected for Lorentz and polarization effects as well as for absorption ($\mu = 52.7\ cm^{-1}$). Conventional heavy-atom techniques were used to solve the structure, and refinement,[11] with all nonhydrogen atoms thermally anisotropic by full-matrix least-squares methods, converged *R* and *r* to their final values of 0.078 and 0.027, respectively.[12] In the final difference Fourier, the highest peak

Table I. Final Atomic Fractional Coordinates and Thermal Parameters with Standard Deviations for $Ru(Me_2dtc)_3I{\cdot}I_2$

Atom	x	y	z	Equiv isotropic B, $Å^2$ [a]
Ru	0.2704 (4)	$^1/_4$	0.0899 (2)	2.1 (1)
S(A1)	0.5035 (14)	$^1/_4$	−0.0514 (7)	2.5 (3)
S(A2)	0.0472 (15)	$^1/_4$	−0.1136 (8)	2.8 (3)
S(B1)	0.0180 (11)	0.1660 (4)	0.1710 (6)	2.9 (2)
S(B2)	0.3593 (11)	0.1149 (3)	0.0723 (6)	2.5 (2)
I(A)	0.5691 (4)	$^1/_4$	0.3189 (2)	2.8 (1)
I(B)	0.5262 (4)	0.4262 (1)	0.4479 (2)	6.6 (1)
C(A)	0.2867 (61)	$^1/_4$	−0.1717 (28)	3.9 (13)
N(A)	0.2869 (57)	$^1/_4$	−0.2924 (25)	4.8 (9)
C(A1)	0.0763 (71)	$^1/_4$	−0.3918 (32)	4.6 (13)
C(A2)	0.4803 (71)	$^1/_4$	−0.3356 (31)	4.0 (11)
C(B)	0.1757 (37)	0.0871 (12)	0.1386 (21)	2.6 (7)
N(B)	0.1070 (31)	0.0114 (11)	0.1658 (16)	2.9 (4)
C(B1)	−0.0511 (39)	−0.0062 (12)	0.2370 (22)	3.2 (8)
C(B2)	0.2745 (41)	−0.0521 (13)	0.1436 (24)	4.8 (6)

Atom	$10^4\beta_{11}$ [b]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru	193 (11)	16 (1)	34 (3)	0	21 (4)	0
S(A1)	161 (30)	30 (4)	30 (8)	0	−7 (12)	0
S(A2)	184 (30)	28 (4)	49 (9)	0	−2 (13)	0
S(B1)	243 (22)	18 (2)	74 (7)	−3 (6)	63 (10)	0 (3)
S(B2)	195 (22)	17 (2)	64 (7)	8 (6)	40 (10)	−1 (3)
I(A)	263 (9)	22 (1)	39 (2)	0	11 (4)	0
I(B)	548 (10)	55 (1)	92 (2)	−9 (3)	−27 (4)	30 (1)
C(A)	475 (153)	31 (16)	−2 (30)	0	−49 (55)	0
N(A)	761 (157)	13 (13)	16 (27)	0	−17 (55)	0
C(A1)	143 (200)	80 (26)	40 (38)	0	−27 (76)	0
C(A2)	348 (211)	51 (19)	56 (39)	0	173 (79)	0
C(B)	168 (80)	11 (10)	72 (25)	41 (22)	−26 (36)	−2 (12)
N(B)	225 (78)	22 (9)	48 (20)	2 (20)	−12 (32)	0 (10)
C(B1)	207 (93)	22 (10)	97 (32)	12 (26)	56 (46)	18 (14)
C(B2)	633 (112)	22 (11)	51 (30)	67 (28)	44 (48)	6 (14)

[a] All atoms refined anisotropically; equivalent isotropic B reported. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

was 1.5 $Å^{-3}$ in the vicinity of the iodine atoms. The highest peak not near an atom was 0.6 $Å^{-3}$.

The final atomic coordinates with their standard deviations and the final anisotropic thermal parameters with their standard deviations are given in Table I. A table of observed and calculated structure factors is available (Table SII of supplementary material).

Results and Discussion

The stoichiometric reaction of $Ru(Me_2dtc)_3$ with iodine in $CHCl_3$ solution was done titrimetrically in an NMR tube. The end point was detected by monitoring the disappearance of the sharp singlet (20.63 ppm downfield from $CHCl_3$) due to $Ru(Me_2dtc)_3$. A 1.0-mol amount of $Ru(Me_2dtc)_3$ was found to react with 1.5 mol of I_2. The new compound formed is not very soluble in chloroform solution and upon standing for a few hours gold needle-shaped crystals precipitated. No thiuram disulfide[13] was produced by the reaction and the elemental analysis of the new complex indicated that the empirical formula is $Ru(Me_2dtc)_3I_3$. The ^1H NMR spectrum of this diamagnetic complex shows a singlet (τ 6.91) in CD_2Cl_2 from −90 to +30 °C. The analogous complexes ($R_2 = Et_2$, Bzl_2 and (Me)(Ph)) also show ^1H NMR spectra which indicate that all identical R groups are magnetically equivalent on the ^1H NMR time scale at −90 °C. The stereochemically nonrigid nature and other spectroscopic properties (UV–VIS and IR) of $Ru(R_2dtc)_3I_3$ (Table SI of supplementary material and Experimental Section) suggest that these complexes and the recently structurally characterized compound $Ru(Et_2dtc)_3Cl$,[5] which is prepared by bubbling HCl through a benzene solution of $Ru(Et_2dtc)_3$,[5,14] are similar in structure.[15]

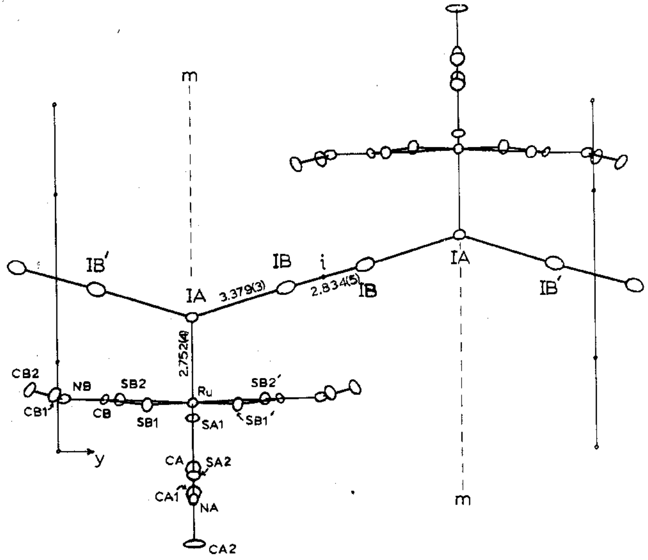

Figure 1. Drawing of the two molecular units in the unit cell of $Ru(Me_2dtc)_3I{\cdot}I_2$ showing the labeling scheme. The crystallographic mirror plane (m) at $y = {}^1/_4$ and the inversion center (i) are shown.

X-Ray Structure of $Ru(Me_2dtc)_3I_3$. The geometry of the molecule, its positioning in the unit cell, and the labeling scheme are shown in Figure 1. This view shows the crystallographic mirror plane at $y = {}^1/_4$ which contains the Ru–I(A) axis of the pentagonal bipyramid (PBP). The near-planarity of the five equatorial sulfur atoms and the ruthenium atom is clearly shown. The displacement of S(A1) below the plane which is caused by the small bite angle of the axial-equatorial dtc ligand (<90°) can also be seen. A stereoscopic view of the unit cell that better shows the ligands is shown in Figure 2. Important interatomic distances and angles are presented in Tables II and III.

Figure 1 shows the infinite planar chains of iodine atoms consisting of alternating solvated I_2 units and collinear coordinated iodine ligands. The solvated I_2 molecule has an I–I bond distance of 2.83 Å which is 0.13 Å longer than the I–I distance in solid molecular I_2,[16] indicating that some do-

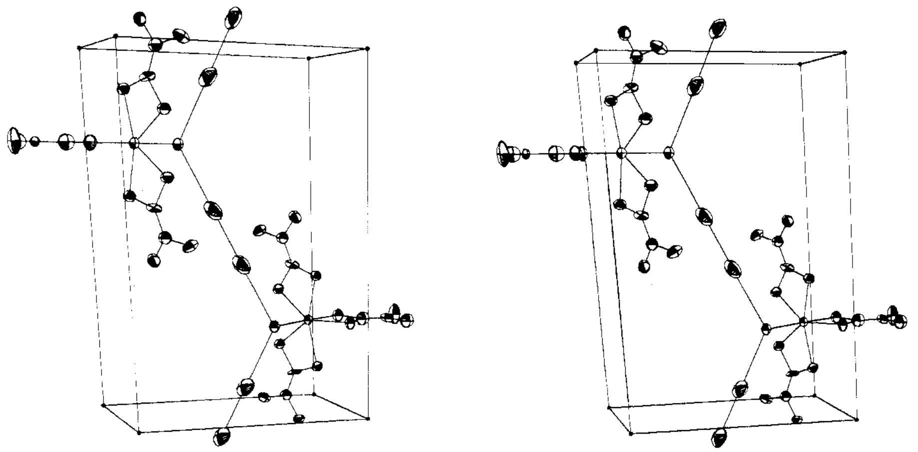

Figure 2. ORTEP stereoview of the entire unit cell for $Ru(Me_2dtc)_3I{\cdot}I_2$. Ellipsoids are 50% probability surfaces.

Table II. Interatomic Distances and Angles in the $RuS_6I{\cdot}I_2$ Core[a]

	Distances, Å		
Ru-S(A1)	2.371 (9)	S(A1)-S(A2)	2.774 (13)
Ru-S(A2)	2.337 (8)	S(B1)-S(B2)	2.760 (10)
Ru-S(B1)	2.459 (7)	S(A1)-S(B2)	2.938 (8)
Ru-S(B2)	2.405 (6)	S(B1)-S(B1)′	2.887 (12)
Ru-I(A)	2.752 (4)	S(A2)-S(B1)	3.488 (11)
I(A)-S(A1)	3.990 (9)	S(A2)-S(B2)	3.387 (8)
I(A)-S(B1)	3.735 (7)	I(A)-I(B)	3.379 (3)
I(A)-S(B2)	3.570 (6)	I(B)-I(B)[b]	2.834 (5)
	Angles, Deg		
S(A1)-Ru-S(A2)	72.2 (3)	S(A2)-Ru-S(B1)	93.3 (3)
S(B1)-Ru-S(B2)	69.1 (2)	S(A2)-Ru-S(B2)	91.2 (2)
S(A1)-Ru-S(B2)	75.9 (2)	I(A)-Ru-S(A1)	102.0 (2)
S(B1)-Ru-S(B1)′	71.9 (3)	I(A)-Ru-S(B1)	91.4 (2)
S(A2)-Ru-I(A)	174.2 (3)	I(A)-Ru-S(B2)	87.4 (2)
Ru-I(A)-I(B)	106.2 (1)	I(B)-I(A)-I(B)′	127.1 (1)
		I(A)-I(B)-I(B)[b]	177.9 (1)

[a] For numbering system, see Figure 1. [b] I(B) through inversion center from central I(B).

Table III. Interatomic Distances and Angles in the Ligands[a]

	Ligand A	Ligand B
	Distances, Å	
S(1)-C	1.65 (3)	1.76 (3)
S(2)-C	1.76 (5)	1.58 (3)
C-N	1.33 (4)	1.42 (3)
N-C(1)	1.50 (5)	1.43 (4)
N-C(2)	1.40 (6)	1.57 (3)
	Angles, Deg	
Ru-S(1)-C	90 (2)	87 (1)
Ru-S(2)-C	89 (1)	93 (1)
S(1)-C-S(2)	109 (2)	111 (1)
S(1)-C-N	127 (3)	117 (2)
S(2)-C-N	124 (3)	132 (2)
C-N-C(1)	121 (3)	126 (2)
C-N-C(2)	123 (3)	111 (2)
C(1)-N-C(2)	116 (3)	121 (2)

[a] For numbering system see Figure 1.

nor–acceptor interaction between the solvated I_2 molecule and the coordinated iodine atom exists. The short and long I–I distances found in this structure are 2.834 (5) and 3.379 (3) Å, respectively, which are different from those found for the unsymmetrical I_3^- (2.83 and 3.03 Å, respectively, in CsI_3)[17] but quite similar to the distances in I_8^{2-} (2.80 and 3.42 Å, respectively, in Cs_2I_8).[18] For a thorough discussion of I···I–I donor–acceptor interactions see the excellent review by Bent.[19]

A number of seven-coordinate PBP complexes of the type M(bidentate)$_3$X have now been structurally characterized.[5-7,20-24] In all of these cases the monodentate ligand X occupies an axial position. Included among these are several complexes which contain dithiocarbamate ligands: $Ru(Et_2dtc)_3Cl$,[5] $Mo(Bu_2dtc)_3NO$,[6] $Re(Et_2dtc)_3CO$,[7] $Mo(Et_2dtc)_3O^+$,[20] and $Ti(Me_2dtc)_3Cl$.[21,25] The distortions from ideal PBP geometry observed in $Ru(Me_2dtc)_3I{\cdot}I_2$ are similar to those found in other $M(R_2dtc)_3X$ complexes. Within the equatorial plane the intraligand chelate "bite" S_{eq}–Ru–S_{eq} angles are slightly smaller than the interligand S_{eq}–Ru–S_{eq} angles, averaging 69.1 and 74.6°, respectively. The average S_{eq}–Ru–S_{eq} angle is 72.4° which is very close to the ideal PBP angle of 72°. The intra- and interligand S_{eq}–S_{eq} pentagon edge distances average 2.76 and 2.92 Å, respectively, all much shorter than the S–S van der Waals contact distance of 3.4 Å. The major distortion from ideal PBP geometry results from the small bite angle in the Me_2dtc ligand which connects an axial and an equatorial site. The S_{ax}–Ru–S_{eq} bite angle of 72.2° is much smaller than 90° which is required by PBP geometry. As a result the ideally linear I(A)–Ru–S_{ax} linkage is slightly bent with an angle of 174.2° and S(A1) is found significantly below the plane formed by the Ru and four equatorial sulfur atoms. This distortion is clearly seen in Figure 1.

The Ru–S distances are very similar to those found in $Ru(Et_2dt)_3Cl$,[5] and the result that Ru–S_{ax} (2.34 Å) is shorter than Ru–S_{eq} (average value 2.41 Å) has been found in all of the $M(R_2dtc)_3X$ structures.[6,7,20,21] These distances are similar to the average Ru–S bond length of 2.38 Å found in $Ru(Et_2dtc)_3$.[26] The observed Ru–I(A) distance of 2.752 (4) Å is slightly longer than the 2.732 (3) Å distance found in $Ru(\eta^5\text{-}C_5H_5)_2I^+$, a Ru(IV) compound in which steric strain has been invoked to account for the long Ru–I bond length.[27] Further evidence that steric crowding affects the Ru–I(A) bond length in $Ru(Me_2dtc)_3I{\cdot}I_2$ is the closeness of iodine to the equatorial sulfur atoms. The I(A)–S_{eq} distances range from 3.570 (6) to 3.990 (9) Å with an average value of 3.720 Å. The van der Waals contact distance for I–S is 4.00 Å.[28] There are no abnormally short intermolecular contacts in the structure except for the I(A)–I(B) distance in the polymeric chain.

Physical and Chemical Properties. The conductivity of $Ru(Me_2dtc)_3I{\cdot}I_2$ and its N-substituted analogues in nitromethane solution (Λ ranges from 63 to 77 Ω^{-1} cm^2 mol^{-1}) indicates some ionic dissociation. The conductances of nitromethane solutions of $[Fe(Et_2dtc)_3]BF_4$,[29] $[Ru_2(Et_2dtc)_5]BF_4$,[30] and $Ru(Et_2dtc)_3Cl$[5] are 87, 90, and 22 Ω^{-1} cm^2 mol^{-1}, respectively. The stereochemically nonrigid nature of $Ru(R_2dtc)_3I{\cdot}I_2$ as indicated by low-temperature ^{1}H NMR, therefore, probably involves dissociation of I_3^- and rearrangement of the cation followed by recombination. This is the same mechanism which has been proposed to account for the nonrigid nature of $Ru(R_2dtc)_3Cl$.[5]

The reaction chemistry of the $Ru(R_2dtc)_3I{\cdot}I_2$ complexes is essentially identical with that of $Ru(Et_2dtc)_3Cl$[5] and will not be discussed in detail here. Several important reactions are the formation of $[Ru_2(R_2dtc)_5]BF_4$[30] upon addition of $AgBF_4$ and the formation of $Ru(R_2dtc)_3$ upon addition of NaR_2dtc both in acetone solution. These reactions illustrate the labile nature of the Ru–I bond.

The addition of I_2 to $Fe(Me_2dtc)_3$ in CH_2Cl_2 solution yielded a black crystalline compound which was identified to be $Fe(Me_2dtc)_2I$.[31] The analogous compound (R = Et) has been prepared by reaction of $Fe(Et_2dtc)_3$ with aqueous HI.[8] These novel square-pyramidal, paramagnetic ($S = {}^3/_2$) complexes do not have analogues with ruthenium, presumably because of the greater tendency of ruthenium toward diamagnetism.

Acknowledgment. This research was supported by Grant CHE-19560 from the National Science Foundation. The help of Professor D. Britton on the x-ray determination is also gratefully acknowledged.

Registry No. $Ru(Me_2dtc)_3I_3$, 60949-75-9; $Ru(Et_2dtc)_3I_3$, 60949-76-0; $Ru((Me)(Ph)dtc)_3I_3$, 60949-77-1; $Ru(Bzl_2dtc)_3I_3$, 60949-78-2; $Fe(Me_2dtc)_2I$, 23672-38-0; $Ru(Me_2dtc)_3$, 31656-15-2.

Supplementary Material Available: Table SI, physical and spectroscopic data for $Ru(R_2dtc)_3I{\cdot}I_2$ complexes, and Table SII, observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(12) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $r = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$; the numerator of 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, I) and Table 3.3.1B (Ru). Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for Ru, I, and S.

(13) R_4tds ($R_2NC(S)SSC(S)NR_2$) is the two-electron oxidation product obtained upon reacting R_2dtc^- with I_2.

(14) The reaction of Cl_2 with $Ru(R_2dtc)_3$ in benzene yields $RuCl_3$ and R_4tds rather than $Ru(R_2dtc)_3Cl$.

(15) Even though the data suggested that $Ru(Me_2dtc)_3I_3$ and $Ru(Et_2dtc)_3Cl$ are structurally similar, an x-ray investigation of the former was carried out due to the different preparative procedures employed[5] and in order to elucidate the nature of the three iodine atoms. In addition, the structural determination of $Ru(Me_2dtc)_3I_3$ was begun before the structure of $Ru(Et_2dtc)_3Cl$ was solved.

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Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Hemochromes with Phosphorus Ligands[1]

William M. Connor and Darel K. Straub*

Received September 20, 1976 AIC60698Z

Hemes (porphinatoiron(II) complexes) readily add two axial ligands to form 6-coordinated hemochromes. Interest in the nonprotein hemochromes arises because they provide simple models of known structure for several iron(II) hemoproteins. Hemochromes with various amines, and with carbon monoxide, have been investigated extensively by electronic[2] and Mössbauer[3-5] spectroscopy. Mössbauer spectroscopy has proven particularly valuable in work with hemochromes, as well as with other classes of iron porphines, since each class has a characteristic isomer shift and quadrupole splitting range.

In order to determine more precisely the effect of π-bonding axial ligands on the isomer shift and quadrupole splitting of hemochromes, several new hemochromes with phosphine and phosphite ligands of varying π-bonding capabilities (chosen to provide π-acceptor strengths between the non-π-bonding cyclic amines such as piperidine and the strongly π-bonding carbon monoxide) have been prepared and characterized by Mössbauer spectroscopy.

Experimental Section

Tri-*n*-butylphosphine was obtained from MC/B Chemicals. All other phosphorus ligands used in this study were gifts from Arapahoe Chemical Co., Boulder, Colo. Bis(piperidine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2pip], bis(pyrrolidine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2pyrr], and bis(tetrahydropyridine)tetrakis(*p*-chlorophenyl)porphinatoiron(II) [PClPPFe·2thp], were prepared by reaction of the hemin chloride with the neat hot amine.[3]

Bis(triethyl phosphite)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2(EtO)$_3$P]. Approximately 0.7 g of the piperidine hemochrome, [PMXPPFe·2pip], was dissolved in 60 ml of triethyl phosphite and held at 100 °C for 10–15 min. The solution was cooled to room temperature and filtered. The filtrate was reduced to a volume of 15–20 ml by vacuum distillation at a maximum temperature of 100 °C. The solution in the distillation flask was cooled to room temperature and the crystalline product which formed was collected on a glass frit. The compound was recrystallized from triethyl phosphite, washed well with pentane, and then dried under vacuum at room temperature for 24 h. Anal. Calcd for $C_{60}H_{66}N_4O_{10}P_2Fe$: C, 64.29; H, 5.93; N, 5.00; P, 5.53. Found: C, 64.02; H, 5.90; N, 5.55; P, 5.48.

Bis(tri-*n*-butylphosphine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2(*n*-Bu)$_3$P]. The same procedure was used to prepare this complex as described for the triethyl phosphite hemochrome. A maximum temperature of 130 °C was attained during the vacuum distillation. Anal. Calcd for $C_{72}H_{90}N_4O_4P_2Fe$: N, 4.70; P, 5.19. Found: N, 4.75; P, 5.25.