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Crystal Structures of Chromium and Tungsten Pentacarbonyl Complexes of N,N′-Dimethylimidazolidine-2-thione

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Abstract

Crystals of chromium and tungsten pentacarbonyl complexes of N,N′-Dimethylimidazolidine-2-thione (T) are isotypic with similar cell dimensions. They are triclinic, space group $P\bar{1}$ (C_i, No. 2), $Z = 2$. For $Cr(CO)_5T$, $a = 8.263(3)$, $b = 9.786(4)$, $c = 9.474(3)$ Å, $\alpha = 84.26(2)$, $\beta = 102.26(2)$, $\gamma = 113.76(2)°$, $V = 685.1(4)$ Å^3, $D_c = 1.562$ g/cm^3; for $W(CO)_5T$, $a = 8.426(1)$, $b = 9.895(1)$, $c = 9.552(1)$ Å, $\alpha = 84.42(1)$, $\beta = 102.46(1)$, $\gamma = 114.56(1)°$, $V = 707.3(1)$ Å^3, $D_c = 2.132$ g/cm^3. The structures, solved with 1453 and 3414, observed Mo-Kα diffractometer data to R factors of 0.082 and 0.032 respectively for the Cr and W compounds, consist of discrete neutral molecules, the metal being six coordinated in a slightly distorted octahedral geometry. The Cr–S and W–S bonds are 2.510(3) and 2.617(2) Å respectively, whereas the M–C(carbonyl) bonds *trans* to the S atoms are shorter at 1.827(10) (M = Cr) and 1.956(6) Å (M = W) compared to the average of Cr–C = 1.89(2) Å and W–C = 2.03(1) Å. The S–M–C angles involving the carbonyl groups that point in the direction of the thione are widened (S–Cr–C = 95.0(3)°; S–W–C = 94.8(2)°), indicating a slight steric effect. The differences between corresponding Cr–X and W–X (X are the donating atoms) of these two complexes indicate a stronger W–S bond than Cr–S. This is also reflected in a longer C–S bond (1.716(7) *vs.* 1.697(12) Å) in the W complex.

Introduction

In our continuing study of metal complexes of dithiocarbamates, we have been trying to synthesize bifunctional dithiocarbamates [1]. The reactions between N,N′-dimethylethylenediamine and CS_2 produced a byproduct N,N′-dimethylimidazolidine-2-thione (thione or T) when insufficient amounts of CS_2 were used [2]. As a result, we started the study of reactions between metal carbonyls and this cyclic thiourea [3].

Reaction between Group VIB metal hexacarbonyl $M(CO)_6$ (M = Cr, Mo, or W) and thione, either at elevated temperature or under ultraviolet irradiation, produced reactive, moderately stable pentacarbonyl thione complexes, $M(CO)_5T$. Because of their reactivity, these compounds might be useful as starting materials for inorganic syntheses. As part of the characterization of these compounds, we have undertaken an X-ray crystal structure analysis of the chromium and tungsten complexes. The Mo compound does not yield suitable crystals under the same condition.

Experimental

The preparation of the pentacarbonylthione complexes has been described in the preceding paper [3].

Unit-cell and intensity data were measured on a Nicolet R3m automated four-circle diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å), a scintillation counter, and a pulse-height analyser. Three standard reflections were repeatedly measured between every 125 reflections. Their intensities fluctuated within 2% of their mean values, indicating a stable crystal. The raw data were processed with a learnt-profile procedure [4], and absorption corrections were applied using an empirical method based on a pseudo-ellipsoidal analysis of azimuthal (ψ) scans of selected strong reflections [5, 6]. Pertinent crystallographic and data processing parameters are given in Table I. The W complex gave strong diffraction peaks at high 2θ angles, and more data were collected for it than for the Cr compound.

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TABLE I. Crystal Data and Parameters Used in Structural Determination.

	$Cr(CO)_5T$	$W(CO)_5T$
Molecular formula	$C_{10}H_{10}CrN_2O_5S$	$C_{10}H_{10}N_2O_5SW$
Molecular weight	322.26	454.11
Crystal system	triclinic	
Space group	$P\bar{1}$ (No. 2)	
Cell constants		
a	8.263(3) Å	8.426(1) Å
b	9.786(4)	9.895(1)
c	9.474(3)	9.552(1)
α	84.26(2)°	84.42(1)°
β	102.26(2)	102.46(1)
γ	113.76(2)	114.56(1)
$F(000)$	328	428
Z	2	2
D_c	1.652 g/cm^3	2.132 g/cm^3
D_m	1.65(1)	2.12(1)
Abs. coeff. μ(Mo-Kα)	9.75 cm^{-1}	84.99 cm^{-1}
Crystal size (mm)	0.36 × 0.20 × 0.16	0.20 × 0.14 × 0.10
Mean μr	0.12	0.70
Transmission factor	0.515–0.894	0.239–0.435
Data collected, 2θ max	$h \pm k \pm l$, 50°	$h \pm k \pm l$, 60°
Unique data measured	1949	3934
Observed data $F_o > 3\sigma(F_o)$, n	1453	3414
Number of variables, p	178	178
$R = \Sigma \Vert F_o \vert - \vert F_c \Vert / \Sigma \vert F_o \vert$	0.082	0.032
Weighting scheme ω =	$[\sigma_{F^2} + 0.0015F^2]^{-1}$	$[\sigma_{F^2} + 0.0005F_2]^{-1}$
$R\omega = [\Sigma\omega(\vert F_o \vert - \vert F_c \vert)^2 / \Sigma \vert F_o \vert^2]^{1/2}$	0.096	0.035
$S = [\Sigma\omega(\vert F_o \vert - \vert F_c \vert)^2/(n-p)]^{1/2}$	1.682	1.018

Structure Solution and Refinement

The structures were solved by the heavy atom and Fourier methods. All non-hydrogen atoms were given anisotropic temperature factors. In the last stages of blocked-cascade [7] least-squares refinement, the methyl and methylene H atoms, geometrically generated by assuming C–H bond fixed at 0.96 Å, were assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL Program package [8]. Analytical expressions of neutral-atom scattering factors from International Tables for X-ray Crystallography were employed, and anomalous dispersion corrections were incorporated [8]. The atomic parameters are given in Tables II and III, and tables of measured and calculated structure factors are available from the authors.

Results and Discussion

The crystals of the title compounds consist of hexa-coordinated $M(CO)_5T$ neutral molecules. The two compounds are isotypic with similar cell dimensions. The ORTEP plot of the Cr complex is shown in Fig. 1. The molecule as a whole does not have any nontrival symmetry, but the $W(CO)_5$- and $Cr(CO)_5$- moieties may have approximate C_{4v} or C_{2v} point group symmetry. The spectroscopic data were assigned assuming this approximation.

Since more data from the W compound were used in the refinement, the standard deviations for its bond lengths and angles are smaller. The comparison of bond lengths and angles for these two compounds are given in Table IV.

The coordination geometry around the metal is a slightly distorted octahedron. It is expected that the W–S and W–C bonds are longer than the Cr–S and Cr–C bonds respectively because of the larger size of the W atom. A noticeable distortion is the fact that the metal–carbonyl bonds *trans* to the metal–S are significantly shorter than others (see Table IV). The longer W–S (2.617(2) Å) bond compared to Cr–S (2.510(3) Å) bond may release steric interaction in the W complex as indicated by the smaller W–S–C(1) (102.6(2)°) angle than the Cr–S–C(1) (104.1(3)°) angle. The organic

TABLE II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2, × 10^3) for the Cr Complex.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cr	2525(2)	3345(2)	1972(2)	43(1)
S	2966(4)	1661(3)	4064(3)	59(1)
O(1)	1873(10)	5369(9)	−468(8)	80(4)
O(2)	6194(10)	5746(9)	3136(9)	97(4)
O(3)	799(11)	4530(8)	3805(9)	86(4)
O(4)	−1120(9)	975(9)	789(9)	91(4)
O(5)	4121(9)	2273(8)	−41(7)	75(4)
N(1)	5008(11)	552(9)	3097(8)	57(4)
N(2)	2223(11)	−992(8)	2894(8)	62(4)
C(1)	3406(12)	364(10)	3332(9)	47(4)
C(2)	4950(16)	−659(12)	2316(12)	72(6)
C(3)	3133(18)	−1826(13)	2440(12)	81(6)
C(4)	6644(13)	1923(13)	3339(12)	76(5)
C(5)	380(16)	−1660(14)	3079(15)	93(6)
C(6)	2133(12)	4590(10)	492(10)	56(4)
C(7)	4830(13)	4827(11)	2717(10)	62(5)
C(8)	1473(13)	4074(10)	3134(11)	56(4)
C(9)	249(12)	1848(11)	1256(10)	55(4)
C(10)	3528(12)	2656(10)	765(10)	52(4)
H2a	5040	−382	1326	90
H2b	5891	−990	2757	90
H3a	3233	−2575	3148	90
H3b	2504	−2289	1527	90
H4a	6815	2409	2395	100
H4b	7680	1627	3771	100
H4c	6537	2602	3974	100
H5a	−139	−1212	3645	110
H5b	243	−2658	3469	110
H5c	−246	−1737	2069	110

U_{eq} = 1/3[trace of orthogonalised *U* matrix].

TABLE III. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2, ×10^3) for the W Complex.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
W	2557.2(3)	3356.3(2)	1974.6(2)	39.1(1)
S	3050(2)	1634(2)	4129(2)	59.1(7)
O(1)	1827(7)	5424(6)	−534(6)	81(2)
O(2)	6345(7)	5899(6)	3145(7)	97(3)
O(3)	796(8)	4574(6)	3897(6)	89(3)
O(4)	−1221(7)	856(6)	762(6)	95(3)
O(5)	4218(7)	2267(6)	−114(5)	75(2)
N(1)	5053(7)	566(5)	3105(5)	58(2)
N(2)	2298(8)	−991(5)	2921(6)	64(2)
C(1)	3463(7)	361(5)	3335(5)	45(2)
C(2)	4979(11)	−623(8)	2312(7)	75(4)
C(3)	3158(11)	−1814(7)	2434(8)	79(4)
C(4)	6655(9)	1921(8)	3336(8)	74(4)
C(5)	459(10)	−1659(9)	3064(9)	93(4)
C(6)	2101(7)	4658(6)	411(6)	53(2)
C(7)	4993(8)	4978(6)	2741(6)	58(2)
C(8)	1452(8)	4137(6)	3237(6)	55(2)
C(9)	156(8)	1745(6)	1225(6)	56(2)
C(10)	3642(7)	2644(6)	669(6)	47(2)
H2a	5057	−341	1331	90
H2b	5906	−946	2736	90
H3a	3259	−2566	3118	90
H3b	2524	−2263	1521	90
H4a	6953	2434	2437	90
H4b	7651	1698	3869	90
H4c	6422	2559	3915	90
H5a	94	−1061	3579	110
H5b	266	−2610	3564	110
H5c	−245	−1839	2087	110

U_{eq} = 1/3[trace of orthogonalised *U* matrix].

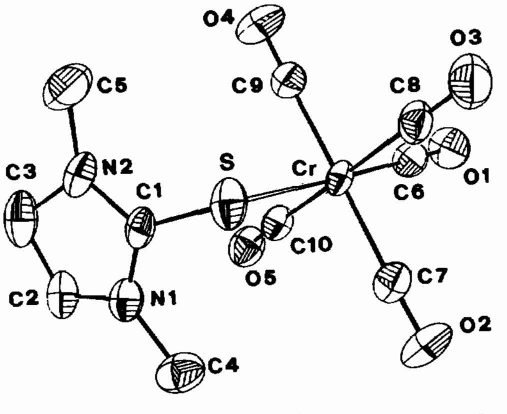

Fig. 1. An ORTEP drawing of the Cr complex. The atomic labelling and shape of the W molecule are the same.

portion of the thione molecule is bent toward the C(10)O(5) carbonyl; the steric effects exhibit themselves in the angles: S–Cr–C(10), 95.0(3)°; S–W–C(10), 94.8(8)°. Similar occurrences have been observed in other S-bonded metal carbonyl complexes [9, 10].

If bond lengths between the metal and the donating atoms are entirely due to the size of the central atom, the differences in these bond lengths should be constant. These differences are given in Table IV. Apparently, the smaller difference between W–S and Cr–S (0.107 Å) compared to those of W–C and Cr–C (ranging from 0.124 to 0.162 Å) indicates a stronger W–S bond than Cr–S bond. Furthermore, the C–S distance of the W compound (1.716(7) Å) is longer than that of the Cr compound (1.697(12) Å). Both of these are longer than the C–S bond of thione in its uncomplexed state [1]. The C–S stretching bands are 495 and 480 cm^{-1} respectively for the Cr and W compounds, in agreement with the same conclusion. The covalent single bond radii of Cr(O), W(O) and S are 1.48 [11], 1.611 [12], and 1.04 Å [13] respectively; thus the observed Cr–S distance 2.510(3) Å is equal to the sum of the radii of Cr and S, but the observed W–S distance

TABLE IV. Comparison of Bond Distances (Å) and Bond Angles (°) for Cr and W Pentacarbonyl Thione Complexes.

Cr(CO)$_5$T		W(CO)$_5$T		
a. Metal–ligand bond lengths				Difference[a]
Cr–S	2.510(3)	W–S	2.617(2)	0.107
Cr–C(6)	1.827(10)	W–C(6)	1.956(6)	0.129
Cr–C(7)	1.908(8)	W–C(7)	2.041(5)	0.133
Cr–C(8)	1.881(12)	W–C(8)	2.045(8)	0.164
Cr–C(9)	1.892(8)	W–C(9)	2.016(5)	0.124
Cr–C(10)	1.859(12)	W–C(10)	2.021(7)	0.162
b. Bond lengths of thione moieties				(Thione)[b]
C(1)–S	1.697(12)	C(1)–S	1.716(7)	1.673(5)
C(1)–N(1)	1.325(14)	C(1)–N(1)	1.333(9)	1.334(5)
C(1)–N(2)	1.335(10)	C(1)–N(2)	1.325(6)	1.342(5)
N(1)–C(2)	1.439(16)	N(1)–C(2)	1.433(11)	1.449(5)
N(2)–C(3)	1.455(20)	N(2)–C(3)	1.454(12)	1.455(5)
C(2)–C(3)	1.497(16)	C(2)–C(3)	1.518(10)	1.517(5)
N(1)–C(4)	1.466(11)	N(1)–C(4)	1.447(7)	1.459(5)
N(2)–C(5)	1.437(15)	N(2)–C(5)	1.441(10)	1.459(5)
c. Bond lengths of carbonyl groups				
C(6)–O(1)	1.168(12)	C(6)–O(1)	1.168(8)	
C(7)–O(2)	1.140(10)	C(7)–O(2)	1.137(7)	
C(8)–O(3)	1.149(16)	C(8)–O(3)	1.136(11)	
C(9)–O(4)	1.135(10)	C(9)–O(4)	1.149(7)	
C(10)–O(5)	1.152(14)	C(10)–O(5)	1.138(9)	
d. Bond angles within the coordination sphere				
SCrC(6)	77.3(4)	SWC(6)	177.1(2)	
C(7)CrC(9)	178.9(4)	C(7)WC(9)	179.6(2)	
C(8)CrC(10)	177.9(4)	C(8)WC(10)	177.8(2)	
SCrC(7)	89.2(3)	SWC(7)	89.7(2)	
SCrC(8)	87.0(3)	SWC(8)	87.4(2)	
SCrC(9)	89.8(3)	SWC(9)	89.9(2)	
SCrC(10)	95.0(3)	SWC(10)	94.8(2)	
C(6)CrC(7)	91.4(4)	C(6)WC(7)	91.1(2)	
C(6)CrC(8)	90.3(5)	C(6)WC(8)	89.8(3)	
C(6)CrC(9)	89.6(4)	C(6)WC(9)	89.2(2)	
C(6)CrC(10)	87.6(5)	C(6)WC(10)	88.0(3)	
C(7)CrC(8)	89.8(5)	C(7)WC(8)	89.6(3)	
C(7)CrC(10)	90.8(4)	C(7)WC(10)	90.2(3)	
e. Other angles involving the coordinating atoms				
CrSC(1)	104.1(3)	WSC(1)	102.6(2)	
CrC(6)O(1)	179.0(9)	WC(6)O(1)	179.2(6)	
CrC(7)O(2)	177.9(9)	WC(7)O(2)	178.6(5)	
CrC(8)O(3)	177.8(9)	WC(8)O(3)	177.6(5)	
CrC(9)O(4)	177.9(8)	WC(9)O(4)	177.8(5)	
CrC(10)O(5)	176.4(9)	WC(10)O(5)	177.1(5)	

[a] Differences between the respective bond lengths of the W and Cr complexes. [b] Bond lengths of the uncomplexed thione crystal.

of 2.617(2) Å is shorter than the sum of 2.65 Å, again supporting the same argument.

The packing of these neutral molecules is shown in Fig. 2. Intermolecular distances are limited to normal van der Waals contacts.

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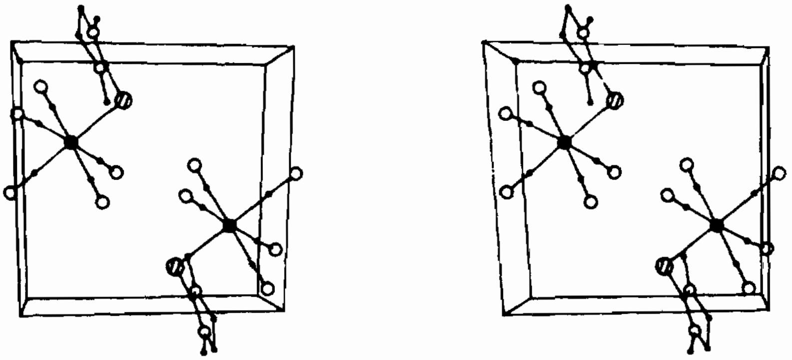

Fig. 2. Stereo packing diagram of the pentacarbonyl thione complexes viewed from a positive *a* axis, *b* down and *c* from left to right.

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