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CRYSTAL AND MOLECULAR STRUCTURE OF AN ORGANIC THIOCYANATE COMPLEX: $(CH_3SCN)Cr(CO)_5$ *

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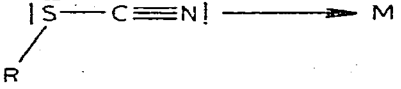
Summary

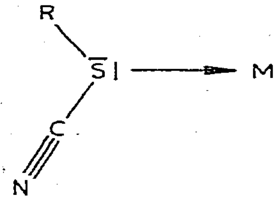
The molecular structure of $(CH_3SCN)Cr(CO)_5$ has been determined by single crystal X-ray diffraction techniques. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.572(1)$, $b = 12.034(3)$, $c = 13.783(3)$ Å, $\beta = 96.48(3)°$ with four molecules per cell. The structure was refined by the full matrix least squares techniques to a final crystallographic discrepancy factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.038 based on 1513 unique observed reflections ($I > 3\sigma(I)$). The methyl thiocyanate ligand was found to be coordinated via the nitrogen atom with structural parameters essentially identical to those of the free, gaseous CH_3SCN. The coordination geometry around the chromium atom is octahedral with the Cr—C distance (1.831(4) Å) to the *trans* CO ligand shorter than those (1.905(4) Å, average) to the *cis* CO groups.

Introduction

There are relatively few known complexes [1] containing organic thiocyanates (RSC≡N) as ligands. In these complexes, either the nitrogen or sulfur atom has been proposed as the donor to the metal as in structures I and II. The assignment



(I)



(II)

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of bonding mode in any given complex is difficult, and tentative assignments have generally been made on the basis of infrared spectra of the complexes. However, all structural assignments have been uncertain as no single-crystal X-ray structural investigations of any organic thiocyanate complexes have been reported.

For a recently synthesized series of RSCN, RSeCN and ROCN complexes of the Group VIB metal carbonyls [1] of the composition $M(CO)_5(NCXR)$, we tentatively assigned structures involving nitrogen coordination on the basis of infrared and ^1H and ^{13}C NMR comparisons. However, since the spectral interpretations were debatable, an X-ray structural investigation of one of these derivatives, $(CH_3SCN)Cr(CO)_5$, was carried out in order to establish unequivocally the nature of the methyl thiocyanate coordination.

Experimental

Crystal data

$(CH_3SCN)Cr(CO_5)$, mol. wt. 265.17, monoclinic $P2_1/n$, $a = 6.572(1)$, $b = 12.034(3)$, $c = 13.783(3)$ Å, $\beta = 96.48(3)°$, $V = 1088.98$ Å^3, $\rho_c = 1.617$ g/cm^3, $Z = 4$, $\mu = 12.8$ cm^{-1} for Mo-K_α.

A crystal of the title compound of dimensions 0.4 × 0.3 × 0.3 mm was grown from pentane solution at −20°C and mounted in a Lindeman glass capillary and subsequently placed in a translational goniometer head. From four preliminary ω-oscillation photographs taken on an automated four-circle X-ray diffractometer at various χ and ϕ settings, eight independent reflections were selected and their coordinates were input to the automatic indexing program ALICE [2].

The resulting reduced cell and reduced cell scalars indicated $2/m$ (monoclinic) symmetry, which was confirmed by inspection of axial ω-oscillation photographs. The observed layer spacings on these photographs were equal, within experimental error, to those predicted for this cell by the indexing program. The lattice constants were obtained from a least squares refinement based on the precise $\pm 2\phi(|2\theta| > 20°)$ measurement of sixteen strong independent reflections. At 27°C using Mo-K_α ($\lambda = 0.70954$ Å) they are $a = 6.572(1)$, $b = 12.034(3)$, $c = 13.783(3)$ Å, and $\beta = 96.48(3)°$.

Collection and reduction of X-ray intensity data

The data were collected at 27°C with graphite-monochromated Mo-K_α radiation on an automated four-circle diffractometer designed and built at Ames Laboratory and previously described by Rohrbaugh and Jacobson [3]. All data (4224 reflections) within a 2θ sphere of 50° ($\sin\theta/\lambda = 0.596$ Å^{-1}) in the hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$ were measured using an ω-step-scan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured every seventy-five reflections. These standard reflections were not observed to vary significantly throughout the entire data collection period (~4 days). Examination of the data revealed systematic absences of $h0l$ reflections for $h + l = 2n + 1$ and $0k0$ reflections for $k = 2n + 1$, thus uniquely defining the space group as $P2_1/n$.

The intensity data were corrected for Lorentz and polarization effects; no absorption correction was made since the minimum and maximum transmission factors were 0.60 and 0.68, respectively. The estimated error in each intensity

TABLE 1

FINAL ATOMIC [a] POSITIONAL AND THERMAL [b] PARAMETERS

Fractional coordinates				Atomic temperature factors					
Atom	x	y	z	β_{11}	β_{12}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	3464(1) [c]	4408(1)	1832(1)	242(2)	63(1)	62(1)	−4(1)	25(1)	−3(1)
S	5493(2)	1602(1)	−415(1)	393(3)	105(1)	72(1)	5(1)	28(1)	−26(1)
N	4285(4)	3303(3)	799(2)	311(8)	81(2)	71(2)	−10(3)	36(3)	−2(2)
C(1)	993(5)	3595(3)	1892(3)	288(9)	82(3)	69(2)	1(4)	24(4)	−1(2)
C(2)	5938(6)	5224(3)	1794(3)	299(10)	87(3)	89(3)	−5(5)	23(4)	−4(2)
C(3)	2134(6)	5379(3)	865(3)	297(10)	83(3)	77(2)	−21(4)	25(4)	−2(2)
C(4)	4817(6)	3512(3)	2843(3)	291(10)	88(3)	79(2)	8(4)	32(4)	2(2)
C(5)	2695(6)	5342(3)	2776(3)	308(10)	81(3)	74(2)	21(4)	25(4)	−2(2)
C(6)	4762(5)	2624(3)	303(2)	322(10)	80(3)	61(2)	−13(4)	31(4)	−6(2)
C(7)	7688(9)	1097(5)	353(4)	461(17)	116(5)	100(4)	43(8)	−4(6)	−27(4)
O(1)	−500(4)	3141(3)	1965(2)	334(8)	128(3)	104(2)	−52(4)	36(3)	1(2)
O(2)	7393(5)	5737(3)	1807(3)	349(9)	133(3)	167(3)	−76(4)	40(4)	−1(3)
O(3)	1357(5)	6012(3)	332(2)	455(10)	103(2)	105(1)	−7(4)	−11(4)	28(2)
O(4)	5616(5)	3033(3)	3489(2)	452(10)	149(3)	105(2)	52(5)	9(4)	35(2)
O(5)	2212(5)	5907(3)	3384(2)	571(11)	114(3)	101(2)	25(5)	72(4)	−33(2)
H(1)	880(7)	163(5)	35(4)	65(13)					
H(2)	725(8)	94(5)	97(4)	69(15)					
H(3)	804(8)	37(5)	5(4)	71(14)					

[a] The positional parameters for non-hydrogen atoms are represented in fractional unit cell coordinates ($\times 10^4$); hydrogen unit cell coordinates are ($\times 10^3$). [b] The β_{ij} are defined by: $T = \exp\{-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{23})\}$. If only β_{11} column is listed, this corresponds to an isotropic temperature factor ($\times 10$). [c] In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.03\ C_T)^2 + (0.03\ C_B)^2$$

where C_T and C_B represent the total count and background count, respectively, and and the factor 0.03 represents an estimate of non-statistical errors. The estimated deviations in the structure factors were calculated by the finite-difference method [4]. Equivalent data were averaged and yielded 1513 reflections with $I_o > 3\sigma(I)$ which were retained for structural solution and refinement.

Solution and refinement

The position of the chromium atom was obtained from an analysis of a standard sharpened three-dimensional Patterson function. The remaining non-hydrogen atoms were found by successive structure factor and electron density map calculations [5]. These atomic positional parameters were subsequently refined using anisotropic thermal parameters by a full matrix least squares procedure [6] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$ to a conventional discrepancy factor of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.048$. The scattering factors used were those of Hanson et al. [7], modified for the real and imaginary parts of anomalous dispersion [8].

Analysis of an electron density difference map revealed the individual methyl hydrogen atom positions. Subsequent least-squares refinements varying the positional and isotropic thermal parameters of the hydrogen atoms yielded R =

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) FOR $(CH_3SCN)Cr(CO)_5$

Cr—N	2.064(3)
Cr—C(1)	1.906(4)
Cr—C(2)	1.905(4)
Cr—C(3)	1.908(4)
Cr—C(4)	1.901(4)
Cr—C(5)	1.831(4)
N—C(6)	1.132(5)
S—C(7)	1.796(6)
C(1)—O(1)	1.137(5)
C(2)—O(2)	1.137(5)
C(3)—O(3)	1.139(5)
C(4)—O(4)	1.138(5)
C(5)—O(5)	1.152(5)
C(6)—S	1.682(4)
C(7)—H(1)	0.973(53)
C(7)—H(2)	0.947(57)
C(7)—H(3)	1.005(58)

TABLE 3

BOND ANGLES (°) FOR $(CH_3SCN)Cr(CO)_5$

C(1)—Cr—C(2)	179.1(7)
C(1)—Cr—C(3)	91.1(2)
C(1)—Cr—C(4)	90.4(2)
C(1)—Cr—C(5)	88.8(2)
C(1)—Cr—N	89.4(1)
C(2)—Cr—C(3)	89.4(2)
C(2)—Cr—C(4)	89.0(2)
C(2)—Cr—C(5)	90.5(2)
C(2)—Cr—N	91.3(2)
C(3)—Cr—C(4)	176.8(2)
C(3)—Cr—C(5)	88.8(2)
C(3)—Cr—N	92.7(1)
C(4)—Cr—C(5)	88.4(2)
C(4)—Cr—N	90.2(2)
C(5)—Cr—N	177.7(2)
Cr—C(1)—O(1)	176.6(3)
Cr—C(2)—O(2)	176.9(4)
Cr—C(3)—O(3)	175.6(4)
Cr—C(4)—O(4)	175.4(4)
Cr—C(5)—O(5)	178.4(4)
Cr—N—C(6)	173.3(3)
N—C(6)—S	178.9(7)
C(6)—S—C(7)	99.5(2)

TABLE 4

LEAST SQUARES PLANES AND DEVIATIONS (Å)

I [a] $-0.37966\,X + 0.58298\,Y - 0.71832\,Z = 0.52057$
II $0.85832\,X + 0.51179\,Y - 0.03662\,Z = 4.33073$
III $-0.34519\,X + 0.62263\,Y - 0.70225\,Z = 4.40121$

Atom	I	II	III
Cr	0.0138 *	0.0016 *	−0.0235 *
S	−0.3836	−0.1690	−4.8681
N	−0.0108 *	−0.0256 *	−2.0869
C(1)	0.0048 *	−1.9040	−0.0116 *
C(2)	0.0044 *	1.9069	−0.0123 *
C(3)	1.9202	0.0267 *	0.0236 *
C(4)	−1.8873	0.0275 *	0.0238 *
C(5)	−0.0122 *	−0.0302 *	1.8081
C(6)	−0.1485	−0.0843	−3.2076
C(7)	−1.9958	0.6164	−4.9650
O(1)	−0.0088	−3.0388	0.0614
O(2)	−0.0106	3.0415	0.0550
O(3)	3.0519	0.0768	0.1325
O(4)	−3.0201	0.0642	0.1406
O(5)	−0.0569	−0.0663	2.9592

[a] The planes are defined by the atoms with an asterisk.

0.043. The scattering factor used for hydrogen was that of Stewart et al. [9].

It was observed that the ten largest reflections suffered from secondary extinction effects, therefore an extinction correction of the form $I_o' = I_o(1 + I_c)$, where k was computed from these reflections, was applied to the observed data. Subsequent refinement on this modified data set yielded a final discrepancy factor of $R = 0.038$ and $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o^2\}^{1/2} = 0.056$.

The final positional and thermal parameters are listed in Table 1 *. The standard deviations were calculated from the inverse matrix of the final least squares cycle. Bond lengths and angles are listed in Tables 2 and 3. Least squares planes are listed in Table 4.

Description and discussion of the structure

The molecular structure of $(CH_3SCN)Cr(CO)_5$ is shown in Fig. 1, while the unit cell is depicted in Fig. 2. As can be seen from Fig. 1, the CH_3SCN ligand is coordinated through the nitrogen atom. The Cr—N bond length (2.064(3) Å) is shorter than that (2.185 Å) in the diethylenetriamine complex [10], *fac*-$(dien)Cr(CO)_3$, but similar to that (2.076 Å) [11] in the diimine complex, $(N_2H_2)[Cr(CO)_5]_2$, in which the hybridization of the N atom is more nearly the same as in CH_3SCN.

The bond lengths and bond angles of the CH_3SCN ligand (Tables 1 and 2) are

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* The table of structure factors has been deposited as NAPS Document No. 02953. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 1.50 for photocopies or $ 5.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

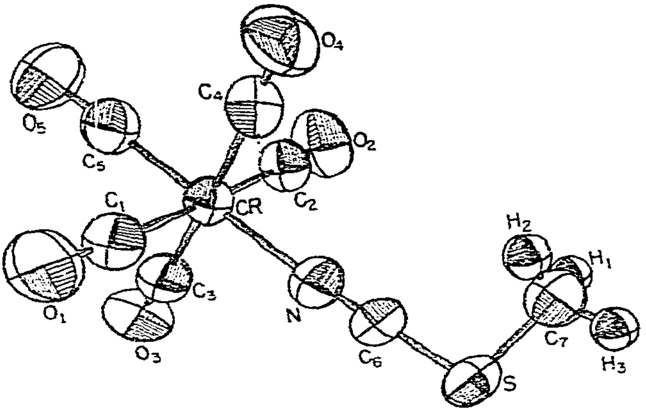

Fig. 1. Molecular configuration of $(CH_3SCN)Cr(CO)_5$.

identical, within experimental error, to those partially determined for gaseous CH_3SCN by microwave spectroscopy [12]. The short (1.132(5) Å) N—C(6) distance implies substantial triple bonding, as illustrated in structure I. The C(6)—S distance is shorter (1.682(4) Å) than S—C(7) (1.796(6) Å), which reflects the smaller size of the *sp* hybridized C(6) as compared to the sp^3 C(7) and possibly also some double bonding between S and C(6). The linear N—C(6)—S bond (178.9°) also supports *sp* hybridization at C(6). The 99.5° C(6)—S—C(7) angle is essentially the same as observed in uncoordinated alkyl thiocyanates [12]. The slightly bent Cr—N—C(6) bond angle (173.3°) is also a common feature of isothiocyanato complexes (M—NCS) [13].

The coordination geometry around the Cr is octahedral with angles between *cis* donor atoms being very close to 90° (Table 3). Also, deviations from the three least squares planes passing through the Cr atom are very small (Table 4).

The Cr—C distance (1.831(4) Å) to the CO *trans* to the CH_3SCN is substantially shorter than those (averaging 1.905(5) Å) to the *cis* CO groups. This shortening of the *trans* Cr—CO bond has been observed in many other metal carbonyl

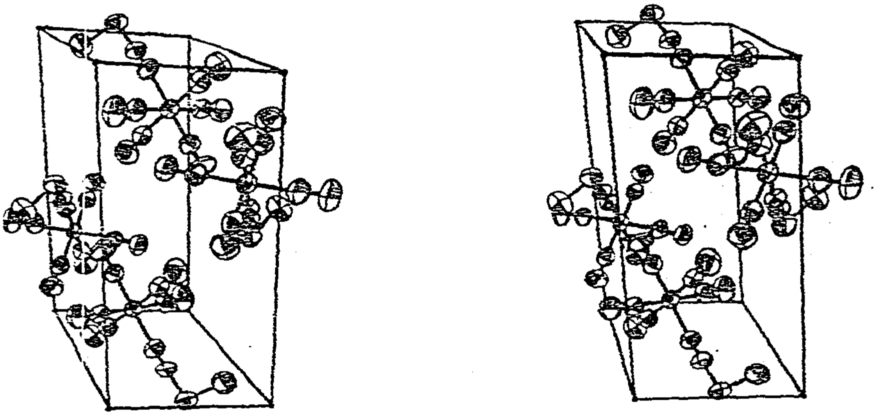

Fig. 2. Unit cell stereograph of $(CH_3SCN)Cr(CO)_5$.

structures [14] and has been attributed to increased π-bonding to a CO *trans* to a poorly π-accepting ligand such as CH_3SCN. As would be predicted from this bonding picture, the C—O distance for the C(5)—O(5) (1.152(5) Å) *trans* to the CH_3SCN appears possibly lengthened (approximately 3σ) as compared to an average value of 1.138(5) Å for the *cis* CO group.

As can be seen from Fig. 2, the closest contacts are between molecules related by the two-fold screw operation; the shortest intermolecular distance being 3.132(5) Å between O(5) and C(6′). Since this distance equals approximately the sum of the Van der Waal's radii, packing effects should produce no appreciable distortions in the molecular geometry.

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