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SULPHUR-CONTAINING METAL COMPLEXES

V *. THE CRYSTAL AND MOLECULAR STRUCTURES OF TETRACARBONYL[*N,N,N'N'*-TETRAMETHYLETHYLENEDIAMINE-*N,N'*]CHROMIUM(0) AND TETRACARBONYL-*cis*-[ETHYL-α-ETHOXY-α-(1,3-DITHIAN-2-YLIDENE)ACETIMIDATE-*N,S*]CHROMIUM(0) **

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Summary

The structures of the title compounds have been determined from three dimensional X-ray data, and they illustrate the significance of hybridization and steric effects on the metal—nitrogen bond strength. The Cr—N(amine) bond lengths average 2.217 Å and the Cr—N(azomethine) distance is 2.095(5) Å. The principal crystallographic data for [$Cr(CO)_4$tmeda] are: space group $P2_1/n$; a 13.45(1), b 11.90(1), c 8.37(1) Å; β 92.5(1)°; $Z = 4$. The crystals of the acetimidate-thioether chelate are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions: a 13.85(1), b 15.31(1), c 9.28(1) Å; β 108.9(1)°. Refinement of the two structures converged to final R indices of 5.2 and 7.0% for 1963 and 2466 independent reflections, respectively.

Introduction

The synthesis of tetracarbonyl(carbene-thioether)chromium(0) complexes of general formula *cis*-[$\overline{\mathrm{Cr}(\mathrm{CO})_4(\mathrm{C}(\mathrm{OEt})\mathrm{C}(\mathrm{OEt}){=}\mathrm{C}(\mathrm{S}}\mathrm{R}^1)\mathrm{R}^2)$] was recently reported [2]. During a synthesis in which the complex BuLi · tmeda (tmeda = *N,N,N',N'*-tetramethylethylenediamine) was used to deprotonate the reagent $PhSCH_2Ph$

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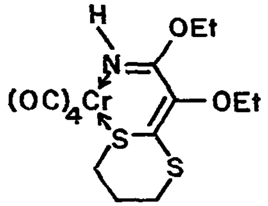
* For Part IV, see ref. 1.
** No reprints available.

prior to the reaction with $[Cr(CO)_6]$, the compound $[Cr(CO)_4tmeda]$(I) was also isolated in a low concentration by column (SiO_2) chromatography. This result suggested the feasibility of replacing the carbene—thioether chelate ring by other bidentate ligands and results from a subsequent study in this connection will appear later. In order to correlate different bond lengths in a disubstituted chromium carbonyl complex containing a bidentate ligand without π-accepting ability with its own and other available infrared data [3], a single-crystal X-ray structure determination of the well-known complex $[Cr(CO)_4tmeda]$ [4] was undertaken.

The reaction of one of the above-mentioned carbene-thioether heterometallocyclic chelates $[R^1R^2 = (CH_2)_3S]$ with *N,N*-dimethylhydrazine, afforded a series of compounds [5]. Infrared and ^1H NMR measurements suggested the following, formally NH-inserted, structure for the main product (II):



While detailed structure information for a large number of chromium carbonyl compounds has now been accumulated [6], no such results for complexes containing the chromium—imidate linkage are available.

A X-ray structural investigation of II was undertaken to establish unambigiously the identity of this species and specifically to confirm that the N-atom plays an important part in the metal—ligand bonding [7,8].

Experimental

Well-shaped yellow and orange crystals of the compounds I (Mol. wt. 280, mass spec.) and II (Mol. wt. 411, mass spec.) respectively, were obtained from ether-pentane solutions (—30°C). The mass spectrum of I indicated the consecutive loss of four carbonyl groups followed by the loss of Me_2NCH_2 (also observed during the fragmentation of the free ligand), as well as the loss of a methyl group (this does not occur in the free ligand), prior to formation of the Cr^+ ion.

Data collection and structure determination

Crystal data: $C_{10}H_{16}O_4CrN_2$ (I), $M = 280.24$. Monoclinic, a 13.45(1), b 11.90(1), c 8.37(1) Å, β 92.5(1)°; D_c 1.39, D_m 1.37 gcm^{-3}; $Z = 4$. Space group $P2_1/n$ ($0k0, k = 2n; h0l, h + l = 2n$). μ(Mo-K_α) 8.01 cm^{-1}. 1963 independent reflections with $\theta \leqslant 23°$, 141 unobservable. Crystal size 0.1 × 0.1 × 0.2 mm; $\omega - 2\theta$ scan, scan width 1.2° (θ), scan speed 0.04° s^{-1}.

$C_{14}H_{17}O_6CrNS_2$ (II), $M = 411.42$. Monoclinic, a 13.85(1), b 15.31(1), c 9.28(1) Å, β 108.9(1)°; D_c 1.47, D_m 1.47 gcm^{-3}; $Z = 4$. Space group $P2_1/n$ ($0k0, k = 2n; h0l, h + l = 2n$). μ(Mo-K_α) 8.01 cm^{-1}. 2466 independent reflections with $\theta \leqslant 23°$, 413 unobservable. Crystal size 0.4 × 0.12 × 0.12 mm.

$\omega - 2\theta$ scan, scan width 0.3°, scan speed 0.015° s^{-1}.

Accurate cell dimensions for both crystals were obtained by least squares refinement of the optimum setting angles of 25 reflections measured on a Philips PW1100 single crystal diffractometer. Intensity data were collected on the same diffractometer. Background for I was counted for 15 s on each side of a reflection. To shorten the collection time for II, which slowly decomposed under irradiation, the background was calculated from a background versus scattering angle curve. Background intensities were measured at systematically absent reflections. Reduction in standard reflection intensity equalled 9%. The loss in intensity due to crystal decomposition was compensated for by 10 scale factors; batches consisted of reflections with equal l, the slowest varying index during data collection. Reflections were regarded as unobserved when $I < 2\sigma(I)$.

Both structures were determined by the heavy atom method, locating the positions of the Cr atoms in Patterson maps and subsequently the other non-hydrogen atoms in Fourier maps. Refinement was by full-matrix least-squares methods. The hydrogen atom positions for I were found in a difference map and refined with a constant temperature factor (U) of 0.097 to give a final R value

TABLE 1

FINAL FRACTIONAL COORDINATES ($\times 10^4$) WITH STANDARD DEVIATIONS IN PARENTHESES FOR COMPLEXES I AND II [a]

$[Cr(CO)_4tmeda]$ (I)				$[Cr(CO)_4[NHC(OEt)C(OEt)=CS(CH_2)_3S]]$ (II)			
Atom	x	y	z	Atom	x	y	z
Cr	2225(1)	1889(1)	299(1)	Cr	5307(1)	3339(1)	6372(1)
N(1)	963(3)	2930(4)	1029(5)	S(1)	4499(1)	2587(1)	7930(2)
N(2)	1501(3)	2194(4)	−2103(5)	S(2)	2943(2)	2935(2)	9508(3)
O(1)	3044(3)	1558(4)	3642(5)	O(1)	5638(5)	5007(4)	8214(7)
O(2)	3759(3)	3768(4)	230(6)	O(2)	7433(4)	2886(4)	8378(6)
O(3)	3908(3)	530(4)	−879(6)	O(3)	6325(4)	4237(3)	4292(6)
O(4)	1332(3)	−410(4)	780(6)	O(4)	5261(4)	1661(3)	4605(6)
C(1)	2726(3)	1691(4)	2345(6)	O(5)	2118(3)	4137(3)	4366(5)
C(2)	3126(4)	3119(5)	218(6)	O(6)	1939(4)	3987(4)	6992(6)
C(3)	3256(4)	1052(5)	−450(7)	N	3822(4)	3711(3)	5083(5)
C(4)	1587(4)	488(5)	565(6)	C(1)	5465(5)	4380(5)	7518(8)
C(5)	550(5)	3467(6)	−498(8)	C(2)	6593(5)	3044(4)	7553(7)
C(6)	526(5)	2693(6)	−1829(7)	C(3)	5905(6)	3853(4)	5083(8)
C(7)	1258(5)	2862(6)	2116(8)	C(4)	5228(5)	2295(4)	5256(7)
C(8)	191(6)	2284(7)	1800(11)	C(5)	2994(5)	3838(4)	5383(7)
C(9)	2088(6)	2962(7)	−3093(8)	C(6)	2844(5)	3674(5)	6863(7)
C(10)	1324(6)	1147(6)	−3048(8)	C(7)	3424(5)	3166(4)	8012(7)
				C(8)	3984(9)	2569(10)	999(15)
				C(9)	4881(8)	2261(8)	1021(12)
				C(10)	5362(6)	2694(7)	9903(10)
				C(11)	2148(5)	4445(5)	2875(8)
				C(12)	1134(7)	4924(6)	2186(10)
				C(13)	1818(9)	4949(7)	7035(13)
				C(14A)	2421(14)	5289(10)	8445(19)
				C(14B)	1493(42)	5195(33)	8110(57)

[a] Estimated standard deviations in the least significant digits are in parentheses.

of 5.2%. For II the hydrogen atom positions could not be located. It was found that C(14) (Fig. 2) exhibited disorder occupying two possible positions. This was compensated for by inserting carbon atoms at both positions and refining the occupancy factors for both with the constraint that their sum had to be unity. The final occupancies turned out to be 0.75 for C(14A) and 0.25 for C(14B). The refinement of II was carried out with the constraint $U_{33} = \frac{1}{2}(U_{11} + U_{22})$ on the anisotropic thermal parameters to eliminate correlations with the scale factors mentioned above. The *R* factor converged to 0.070 with unit weights. The position of C(8) in II (Fig. 2) could not be reliably found, as reflected by the very high thermal parameters and the apparently anomalous bond lengths C(8)—C(9) and C(8)—S(2) [9]. Closer inspection of a difference map calculated with C(8) removed, revealed an extensive domain of residual electron density, about 1.5 Å in diameter, indicating a positional uncertainty very much larger than the standard deviations calculated from the least squares matrix. Little attention should thus be given to the bonding parameters in which this very labile atom participates.

The calculations were performed with the X-ray system of crystallographic computer programs [10]. Lists of the observed and calculated structure factors and anisotropic thermal parameters for both structures as well as final positional parameters for the hydrogen atoms of compound I, are available from

TABLE 2

BOND DISTANCES AND ANGLES FOR COMPLEX I [a]

Bond lengths (Å)			
Cr—N(1)	2.209(4)	N(2)—C(6)	1.467(7)
Cr—N(2)	2.225(4)	N(2)—C(9)	1.489(8)
Cr—C(1)	1.827(5)	N(2)—C(10)	1.489(8)
Cr—C(2)	1.903(6)	C(1)—O(1)	1.160(6)
Cr—C(3)	1.840(6)	C(2)—O(2)	1.150(6)
Cr—C(4)	1.893(6)	C(3)—O(3)	1.144(6)
N(1)—C(5)	1.512(7)	C(4)—O(4)	1.139(6)
N(1)—C(7)	1.477(7)	C(5)—C(6)	1.444(9)
N(1)—C(8)	1.465(8)	Av. C—H	1.048(66)
Bond angles (degrees)			
N(2)—Cr—N(1)	81.2(1)	C(7)—N(1)—C(5)	106.4(5)
C(1)—Cr—N(1)	94.0(2)	C(8)—N(1)—Cr	113.3(4)
C(1)—Cr—N(2)	175.1(2)	C(8)—N(1)—C(5)	110.6(5)
C(2)—Cr—N(1)	94.4(2)	C(8)—N(1)—C(7)	107.4(5)
C(2)—Cr—N(2)	95.5(2)	C(6)—N(2)—Cr	106.5(3)
C(2)—Cr—C(1)	85.6(2)	C(9)—N(2)—Cr	112.5(4)
C(3)—Cr—N(1)	176.1(2)	C(9)—N(2)—C(6)	109.8(5)
C(3)—Cr—N(2)	95.0(2)	C(10)—N(2)—Cr	113.4(4)
C(3)—Cr—C(1)	89.9(2)	C(10)—N(2)—C(6)	107.4(5)
C(3)—Cr—C(2)	85.0(2)	C(10)—N(2)—C(9)	107.2(5)
C(4)—Cr—N(1)	95.9(2)	O(1)—C(1)—Cr	179.5(4)
C(4)—Cr—N(2)	93.8(2)	O(2)—C(2)—Cr	171.5(5)
C(4)—Cr—C(1)	85.8(2)	O(3)—C(3)—Cr	178.3(5)
C(4)—Cr—C(2)	167.0(2)	O(4)—C(4)—Cr	170.5(5)
C(4)—Cr—C(3)	85.2(2)	C(6)—C(5)—N(1)	112.2(5)
C(5)—N(1)—Cr	105.2(3)	C(5)—C(6)—N(2)	112.9(5)
C(7)—N(1)—Cr	113.7(3)		

[a] Estimated standard deviation in the least significant digits are in parentheses.

TABLE 3

INTRAMOLECULAR BOND LENGTHS AND ANGLES FOR COMPLEX II [a]

Bond lengths (Å)			
Cr—C(1)	1.890(8)	C(6)—O(6)	1.383(7)
Cr—C(2)	1.819(7)	C(6)—C(7)	1.353(9)
Cr—C(3)	1.838(7)	C(7)—S(1)	1.757(7)
Cr—C(4)	1.888(7)	C(7)—S(2)	1.760(7)
Cr—N	2.095(5)	C(8)—C(9)	1.323(12)
Cr—S(1)	2.392(2)	C(8)—S(2)	1.736(11)
C(1)—O(1)	1.138(8)	C(9)—C(10)	1.552(11)
C(2)—O(2)	1.165(7)	C(10)—S(1)	1.840(9)
C(3)—O(3)	1.159(7)	O(5)—C(11)	1.475(8)
C(4)—O(4)	1.151(7)	C(11)—C(12)	1.529(10)
N—C(5)	1.281(7)	O(6)—C(13)	1.485(11)
C(5)—C(6)	1.476(8)	C(13)—C(14A)	1.404(18)
C(5)—O(5)	1.352(7)	C(13)—C(14B)	1.277(51)
Bond angles (degrees)			
S(1)—Cr—C(1)	93.3(2)	O(6)—C(6)—C(7)	117.0(6)
S(1)—Cr—C(2)	94.3(2)	C(6)—C(7)—S(1)	123.5(5)
S(1)—Cr—C(3)	176.1(2)	C(6)—C(7)—S(2)	117.1(5)
S(1)—Cr—C(4)	88.2(2)	S(1)—C(7)—S(2)	118.4(4)
S(1)—Cr—N	84.9(1)	C(7)—S(2)—C(8)	105.3(4)
C(1)—Cr—C(2)	87.6(3)	S(2)—C(8)—C(9)	131.3(10)
C(1)—Cr—C(3)	90.6(3)	C(8)—C(9)—C(10)	116.2(9)
C(1)—Cr—C(4)	176.9(3)	C(9)—C(10)—S(1)	110.2(7)
C(1)—Cr—N	90.3(3)	C(10)—S(1)—C(7)	101.4(4)
C(2)—Cr—C(3)	86.5(3)	Cr—S(1)—C(7)	110.6(2)
C(2)—Cr—C(4)	89.5(3)	Cr—S(1)—C(10)	106.2(3)
C(2)—Cr—N	177.7(3)	Cr—C(1)—O(1)	174.6(7)
C(3)—Cr—C(4)	87.9(3)	Cr—C(2)—O(2)	176.9(6)
C(3)—Cr—N	94.5(2)	Cr—C(3)—O(3)	175.8(6)
C(4)—Cr—N	92.6(2)	Cr—C(4)—O(4)	174.7(6)
Cr—N—C(5)	134.4(4)	C(5)—O(5)—C(11)	118.1(5)
N—C(5)—O(5)	124.3(6)	O(5)—C(11)—C(12)	104.1(6)
N—C(5)—C(6)	125.7(6)	C(6)—O(6)—C(13)	117.3(6)
O(5)—C(5)—C(6)	110.0(5)	O(6)—C(13)—C(14A)	110.8(11)
C(5)—C(6)—O(6)	115.3(6)	O(6)—C(13)—C(14B)	112.6(24)
C(5)—C(6)—C(7)	127.2(6)		

[a] Estimated standard deviations in the least significant digits are in parentheses.

TABLE 4

DISTANCES (Å) FROM LEAST-SQUARES PLANE IN COMPLEX II

Plane	Deviation
Cr [a]	0.013
S(1) [a]	−0.049
N [a]	0.047
C(2) [a]	0.053
C(3) [a]	−0.063
O(2)	0.098
O(3)	−0.158
C(5)	0.477
C(6)	1.035
C(7)	0.884
O(5)	0.468
O(6)	1.627
S(2)	1.411
C(10)	0.962
Angle [b]	1.1°

[a] Atoms contributing to plane. [b] Angle between line C(1)—C(4) and normal to plane.

the authors (G.J.K.) on request. Structural results are given in the tables: atomic coordinates in Table 1, bond lengths and angles in Tables 2 and 3 and details of selected least square planes through atomic positions in Table 4.

Results and discussion

The perspective overall molecular geometries of the two complexes and the numbering systems adopted, are illustrated in Figs. 1 and 2 and a stereoview of the cell of II is given in Fig. 3. Both *cis*-disubstituted carbonyl complexes contain bidentate ligands in octahedral metal complexes.

In structure I all the non-metal atoms in the five membered chelate ring are approximately sp^3 hybridised as anticipated, and therefore the average length of 1.490 Å for the N(1)—C(5) and N(2)—C(6) bonds is longer than the value recently reported for a single bond between a sp^2 hybridised carbon and coordinated N atom (av. 1.452 Å) in the complex tetracarbonyl[*N*,*N*′,*N*″,*N*‴-tetramethylbis(imidazoline-2-ylidene)*N*,*N*″]chromium(0) [11]. However the average Cr—N and Cr—C(0) (*trans*) bond lengths of 2.217 and 1.834 Å are comparable to the corresponding distances (2.199 and 1.820 Å) in such a complex. As mentioned by Brown for other substituted carbonyl complexes of chromium [6], the two mutually *trans* carbonyl groups are bent away from the bidentate ligand. This effect leads to a C(2)—Cr—C(4) angle of 167.0(2)°. It is even more pronounced than in the above mentioned case of $[(CO)_4Cr(NMe(CH_2)_2NMeC{=}CNMe(CH_2)_2NMe)]$. The distortion from local octahedral symmetry

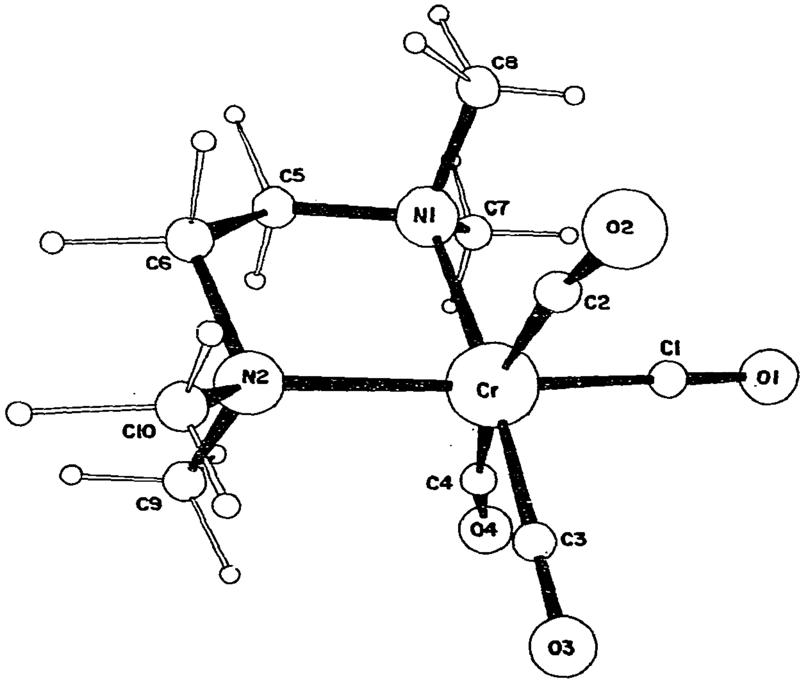


Fig. 1. Perspective view of the $[Cr(CO)_4tmeda]$ complex, showing the numbering scheme adopted. For the sake of clarity the different atoms are represented by arbitrarily small spheres.

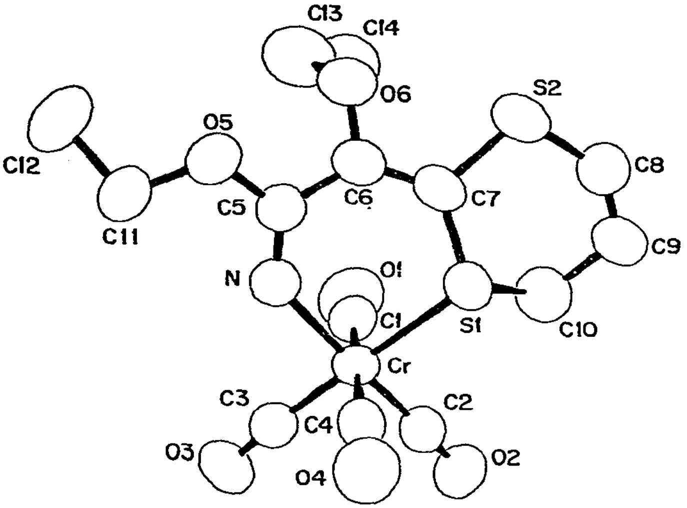


Fig. 2. A view of the $[\overline{\mathrm{Cr(CO)_4(NHC(OEt)C(OEt){=}C}}\underline{\mathrm{S(CH_2)_3S}})]$ molecule prepared with the program ORTEP. The atom numbering scheme is defined. For clarity C(14B) is omitted.

probably results from steric restrictions imposed by the methyl groups bonded to the two N donor atoms.

In complex II the nitrogen atom of the imidate moiety is approximately sp^2 hybridised (the Cr—N—C(5) angle is 134.4(4)°). The Cr—N separation of 2.095(5) Å is appreciably shorter than the corresponding metal—donor-atom bond length in complex I. It is however, longer than the 2.059(2) Å distance in $[(CO)_5Cr(NCSMe)]$ [12] which contains an *sp* hybridised nitrogen atom. The basicity of amines is, among others, a function of the hybridization of the nitrogen atom because hybridization effects electronegativity and therefore, the availability of the lone pair electrons [13]. The strength of the Cr—N bond in the complexes I (N atom sp^3 hybridised), II (N atom sp^2 hybridised) and

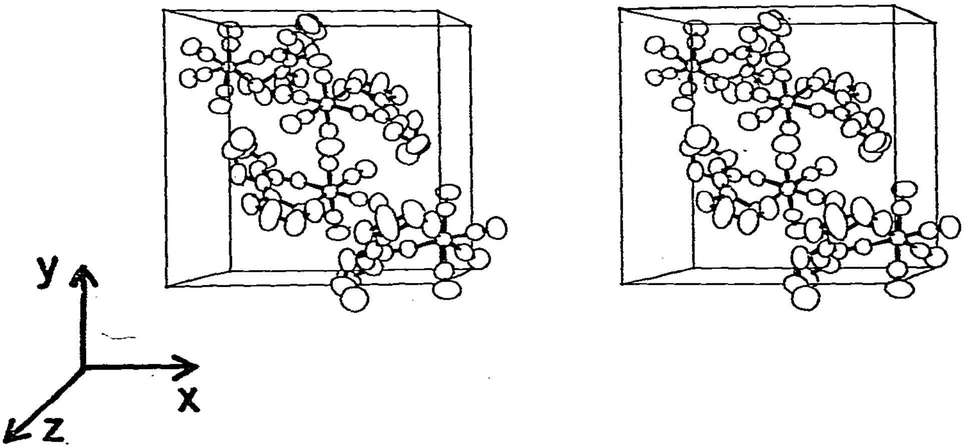


Fig. 3. Stereoview of the crystal packing in the unit cell of $[\overline{\mathrm{Cr(CO)_4(NHC(OEt)C(OEt){=}C}}\underline{\mathrm{S(CH_2)_3S}})]$. The position C(14B) is omitted.

$[(CO)_5Cr(NCSMe)]$ (N atom *sp* hybridised), does not follow the expected trend of becoming weaker with increasing *s*-character in the lone pair orbitals of the donor atom and thus decreasing basicity of the ligands. The experimental result above has to be explained on the basis of more effective overlap between the metal and nitrogen orbitals (containing the lone pair) with increasing *s*-character in the latter [14] enhanced also by decreasing steric influence.

The two carbonyl groups *cis* to the heteroatom ligand in complex II are less affected sterically by the ligand compared to complex I and the C(1)—Cr—C(4) angle is 176.9(3)°. The N—C(5) bond length (1.281(7) Å) indicates a localised double bond which can be compared with that in uncoordinated azomethines (1.29—1.31 Å) [15]. The other double bond between C(5) and C(6), 1.476(8) Å, is also localised. Despite the conjugation present in the chelate ring, the three carbon atoms C(5), C(6) and C(7) are displaced from the plane through the two heteroatom donor atoms, the Cr atom and the carbon atoms of the *trans* carbonyl groups, by more than 0.477 Å (Table 4). The 1,3 dithian ring is in a chair conformation and the Cr—S bond length of 2.392(2) Å is comparable to that (2.384(4) Å) in a five membered chelate ring [9]. Despite the shorter Cr—N distance in compound II compared to I, the *trans*-Cr—C(0) bond lengths (respectively 1.819(7) and av. 1.834 Å) do not differ significantly. Consistent with the π-bonding model, the Cr—C(0) bond lengths in II decrease in the series: *trans* to CO(av. 1.889) > S(1.838(7)) > N(1.819(7) Å). Concomitantly the average C—O distance of a carbonyl ligand *trans* to another CO (1.145 Å) is shorter than the distance *trans* to a sulphur donor atom (1.159(7) Å) and this is shorter than the distance *trans* to the nitrogen donor atom (1.165(7) Å).

There is no evidence for intermolecular hydrogen bonding in II, although two short N···OC approaches (N···O(2) 3.225 Å and N···O(3) 3.363 Å, see Figs. 2 and 3) can be recognised. The two oxygen atoms are respectively transferred by the operators $1.5 + x$, $1.5 + y$, $1.5 + z$, and $1 - x$, $1 - y$, $1 - z$.

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