Of particular interest to our resonance Raman studies is the nature of the Co^{II}—S bonding in the title complex. Within experimental error, one thiourea group is planar while the second deviates from planarity. Atom displacements (in Å) from the least-squares planes are −0·017 (6), −0·02 (2), −0·02 (2) and 0·06 (2), respectively, for the S(1), N(1), N(2), C(1) unit and 0·002 (5), 0·00 (2), 0·00 (2) and −0·01 (2), respectively, for the S(2), N(3), N(4), C(6) unit. Bonding of Co^{II} to a thiourea can involve an sp^2 orbital localized on the S atom as well as a delocalized π-symmetry molecular orbital. Bonding of the former type is characterized by a Co—S—C/S—C—N dihedral angle in the range 17 to 34°; bonding of the latter type was indicated by a considerably larger dihedral angle (75·8°) reported for $Co[SC(NH_2)_2]_4(NO_3)_2.H_2O$ (Spofford, Boldrini, Amma, Carfagno & Gentile, 1970). While sp^2-type bond angles for thiourea complexes normally span the range 108–116°, the Co—S—C angle associated with the large dihedral angle above was 103·0°. The four Co—S—C/S—C—N angles in the title complex range from 36 to 48° while the two unique Co—S—C angles are 104·1 (7) and 103·5 (6)°. Thus, Co—S bonding in the title complex appears to lie at the boundary where 'pure' sp^2 bonding becomes mixed with π-symmetry Co—thiourea interactions.

The ClO_4^- ions appear to be loosely held in lattice holes by Coulombic forces and weak hydrogen bonds to neighboring amine groups. All O atoms involved in hydrogen bonding have relatively small temperature factors. Conversely, those O atoms far removed from the N atoms or which make poor hydrogen-bonding angles have large temperature factors.

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Structure of *cis*-Di-μ-methoxo-bis(η^5-cyclopentadienylnitrosylchromium)

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Abstract. $[Cr_2(CH_3O)_2(C_5H_5)_2(NO)_2]$, $C_{12}H_{16}Cr_2N_2O_4$, orthorhombic, *Pnma*, $a = 12.810\,(7)$, $b = 17.575\,(6)$, $c = 6.431\,(3)$ Å, $Z = 4$, $V = 1447.8$ Å^3, $M_r = 356.2$, $D_c = 1.63$ Mg m^{-3}, $F(000) = 728$, μ(Mo $K\alpha$) $= 1.58$ mm^{-1}, $R = 0.068$ for 718 reflections. The molecule has a plane of symmetry passing through the O and C atoms of the bridging methoxo groups. The Cr_2O_2 ring is buckled, with the two Cr_2O planes inclined at 156°. The Cr—O lengths are 1·955, 1·960 (6) Å and the Cr—Cr distance is 2·882 (2) Å. The O—Cr—O angle is 83·0 (3)° and the Cr—O—Cr angles are 94·6 (4), 95·0 (3)°.

Introduction. The four-membered ring M_2X_2 is a common feature of binuclear metal complexes. The preparation of the complexes $[(\eta^5\text{-}C_5H_5)Cr(NO)X]_2$, where *X* = SPh, NMe_2, *etc.* (Ahmad, Bruce & Knox, 1966) made available an opportunity to examine the effect on the ring geometry of changes in the bridging ligand *X*, and the molecular structures of *trans*-[(η^5-

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$C_5H_5)Cr(NO)SPh]_2$ (McPhail & Sim, 1968) and *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Cr(NO)NMe_2]_2$ (Bush & Sim, 1970) have been described. We now report an X-ray diffraction study of *cis*-$[(\eta^5\text{-}C_5H_5)Cr(NO)OMe]_2$.

The cell dimensions were determined from angular measurements obtained on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. Intensities were measured by the ω–2θ step-scan procedure and 718 independent reflections in the range $\theta \leq 26°$ satisfied the criterion $I > 2\sigma(I)$.

The asymmetric unit comprises half the molecule. Analysis of the Patterson synthesis gave the coordinates of the Cr atom and established that a crystallographic plane of symmetry passes through the methoxo ligands. The C, N and O atoms were located in an electron-density distribution and the atomic parameters were then adjusted by least-squares calculations. Full-matrix refinement with isotropic thermal parameters gave $R = 0{\cdot}100$, after which anisotropic parameters were introduced and R decreased to 0·076. A difference synthesis revealed the H atoms and, when these were included with $B = 3$ Å^2, R became 0·070. Finally, the H atom coordinates were included in the refinement which converged at $R = 0{\cdot}068$, $R_w = 0{\cdot}058$. The weighting scheme was $w = 1/\sigma^2(F)$. Calculations were performed at the Atlas Computer Laboratory with the XRAY 63 program system.*

Discussion. The molecular structure and atomic numbering are shown in Fig. 1 and the arrangement of molecules in the cell is illustrated in Fig. 2. The atomic coordinates, bond lengths and angles are listed in Tables 1 and 2.

The Cr_2O_2 ring is not planar, the Cr and O atoms being alternately 0·14 Å above and below the mean

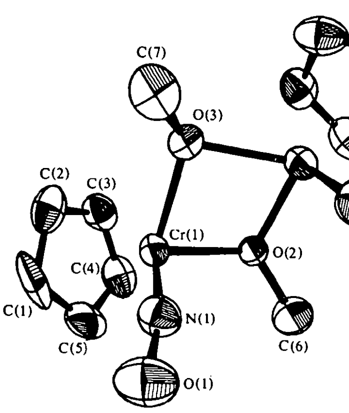

Fig. 1. The molecular structure with atomic labels.

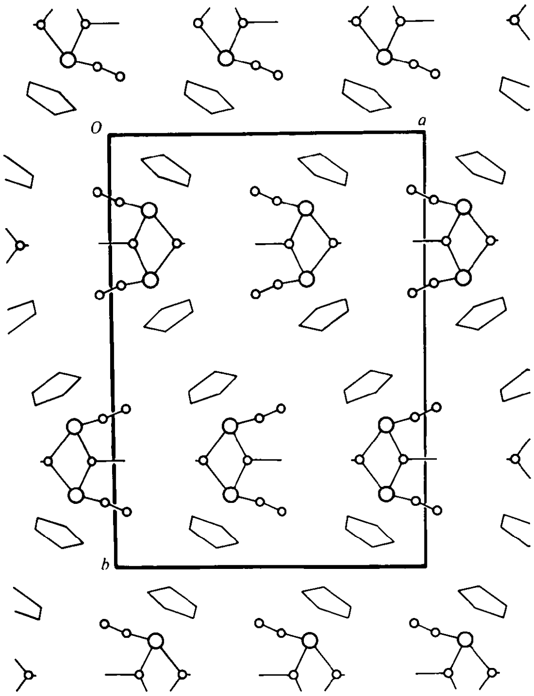

Fig. 2. The crystal structure, viewed in projection along **c**.

Table 1. *Atomic coordinates* (×10^4)

	x	y	z
Cr(1)	1231 (1)	1680 (1)	1264 (2)
O(1)	−354 (6)	1316 (4)	−1724 (10)
O(2)	693 (7)	2500 (–)	3016 (12)
O(3)	2083 (7)	2500 (–)	83 (13)
N(1)	280 (6)	1559 (4)	−525 (11)
C(1)	1692 (12)	466 (6)	895 (22)
C(2)	2589 (10)	887 (6)	1379 (20)
C(3)	2494 (10)	1198 (6)	3299 (18)
C(4)	1533 (10)	981 (6)	4128 (19)
C(5)	1029 (10)	545 (6)	2672 (24)
C(6)	−365 (13)	2500 (–)	3693 (29)
C(7)	2348 (16)	2500 (–)	−2040 (26)

Table 2. *Bond lengths* (Å) *and angles* (°)

Cr(1)–Cr(2)	2·882 (2)	O(2)–C(6)	1·423 (19)
Cr(1)–N(1)	1·689 (8)	O(3)–C(7)	1·407 (19)
Cr(1)–O(2)	1·955 (6)	N(1)–O(1)	1·199 (10)
Cr(1)–O(3)	1·960 (6)	C(1)–C(2)	1·402 (18)
Cr(1)–C(1)	2·227 (11)	C(1)–C(5)	1·431 (20)
Cr(1)–C(2)	2·231 (12)	C(2)–C(3)	1·356 (17)
Cr(1)–C(3)	2·247 (12)	C(3)–C(4)	1·395 (17)
Cr(1)–C(4)	2·248 (12)	C(4)–C(5)	1·371 (18)
Cr(1)–C(5)	2·206 (12)		

O(2)–Cr(1)–O(3)	83·0 (3)	C(4)–C(5)–C(1)	108·7 (11)
Cr(1)–O(2)–Cr(2)	95·0 (3)	Cr(1)–N(1)–O(1)	166·3 (7)
Cr(1)–O(3)–Cr(2)	94·6 (4)	Cr(1)–O(2)–C(6)	120·8 (5)
C(2)–C(1)–C(5)	104·9 (11)	Cr(1)–O(3)–C(7)	120·7 (5)
C(1)–C(2)–C(3)	110·0 (12)	O(2)–Cr(1)–N(1)	103·3 (4)
C(2)–C(3)–C(4)	108·5 (11)	O(3)–Cr(1)–N(1)	103·3 (4)
C(3)–C(4)–C(5)	107·9 (11)	Cr(2)–Cr(1)–N(1)	97·2 (3)

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* Lists of structure factors, thermal factors and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34320 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane of the ring. The fold about the Cr—Cr line is 156° whereas the corresponding angle for the Cr_2N_2 ring of *cis*-[(η^5-C_5H_5)Cr(NO)NMe_2]$_2$ is 178°. The greater puckering of the methoxo complex can be attributed to its less symmetrical pattern of steric strain, for the methoxo complex has methyl groups on only one side of the Cr_2O_2 ring and the dimethylamido complex has pairs of methyl groups above and below its Cr_2N_2 ring. Several related *trans* complexes have crystallographic centres of symmetry and their Cr_2X_2 rings are therefore necessarily planar, *trans*-[(η^5-C_5H_5)Cr(NO)SPh]$_2$ (McPhail & Sim, 1968), *trans*-[(η^5-C_5H_5)Cr(NO)NMe_2]$_2$ (Bush & Sim, 1970), and *trans*-[(η^5-C_5H_5)Cr$(NO)_2$]$_2$ (Calderón, Fontana, Frauendorfer & Day, 1974).

The Cr—Cr separation in the methoxo-bridged complex is 2·882 (2) Å. This is appreciably greater than the 2·62 Å in *trans*-[(η^5-C_5H_5)Cr$(NO)_2$]$_2$, 2·67 Å in *trans*-[(η^5-C_5H_5)Cr(NO)NMe_2]$_2$, and 2·72 Å in *cis*-[(η^5-C_5H_5)Cr(NO)NMe_2]$_2$ but is shorter than the 2·95 Å in *trans*-[(η^5-C_5H_5)Cr(NO)SPh]$_2$. Unbridged Cr—Cr single-bond distances are 2·97 Å in the binuclear $[Cr_2(CO)_{10}]^{2-}$ anion (Handy, Ruff & Dahl, 1970) and 3·28 Å in [(η^5-C_5H_5)Cr$(CO)_3$]$_2$ (Adams, Collins & Cotton, 1974).

The M—M', M—X, M—X—M', and X—M—X' lengths and angles of a central M_2X_2 ring are not independent and the metal–metal separation must be considered in relation to the other dimensions of the ring. Since the single-bond covalent radii of S, sp^3-N and O are *ca* 1·04, 0·71, and 0·66 Å, the mean Cr—S, Cr—N, and Cr—O distances of 2·32, 2·01, and 1·96 Å in the complexes [(η^5-C_5H_5)Cr(NO)X]$_2$ are clearly consistent. The X—M—X' angles in the S-, N- and O-bridged complexes are 101, 95, and 83°, respectively, while the M—X—M' angles are 79, 84, and 95°, respectively. The smaller X—M—X' angles in the dimethylamido and methoxo complexes serve to counterbalance to some extent the reductions in the Cr—Cr distance that would result from the replacement of the S atom in the Cr_2S_2 fragment by the distinctly smaller N or O atoms. The appreciable difference between the ring angles in the dimethylamido and methoxo complexes, together with the concomitant difference in the Cr—Cr distance, is surprising, however.

It has been noted that when the angle at the metal atom in an M_2X_2 ring is obtuse and that at the bridging ligand is acute, the ring generally has a metal–metal bond and, conversely, when the ring lacks a metal–metal bond this arrangement of angles is reversed (Dahl, de Gil & Feltham, 1969; Connelly & Dahl, 1970; Simon & Dahl, 1973). If this test is applied to the [(η^5-C_5H_5)Cr(NO)X]$_2$ complexes, the angular pattern suggests that the O-bridged complex differs from the S- and N-bridged complexes by lacking a direct metal–metal bond. Nevertheless, all these complexes are diamagnetic and metal–metal spin coupling must be a common feature. It is possible, of course, that superexchange interaction through the bridging ligands may be important in the methoxo complex.

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The Structure of Dichloro-DL-ethioninepalladium(II)

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Abstract. Pd($C_6H_{13}NO_2S$)Cl_2, M_r = 340·547, monoclinic, $P2_1/n$, a = 11·065 (11), b = 14·539 (12), c = 7·138 (4) Å, β = 97·60 (4)°, U = 1138 (2) Å^3, Z = 4, D_m = 1·96, D_c = 1·98 Mg m^{-3}, μ = 2·20 mm^{-1}. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares to R =