Crystal and Molecular Structure of *trans*-Dichlorobis-(*N*-methylsalicylaldiminato)molybdenum(IV)

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The title compound crystallizes in space group $P2_1/c$ with $a = 6{\cdot}429(6)$, $b = 13{\cdot}619(14)$, $c = 10{\cdot}047(10)$ Å, $\beta = 107{\cdot}88(1)°$, $Z = 2$. The structure has been determined by Patterson and Fourier methods and refined to R 0·057 from three-dimensional diffractometer data (1325 observed reflections). Its structure consists of discrete monomeric units which are required crystallographically to be centrosymmetric. The two chlorine atoms are in a *trans* arrangement and the bond distances Mo–Cl, Mo–O, and Mo–N are respectively 2·39, 1·95, and 2·14 Å.

MANY chelate complexes of the type $M(chel)_2X_2$ † (where chel = sal-NR, ½salen, ½acacen, acac, or oxine; X = Cl, Br, or I) have now been prepared and both *cis*- and *trans*-stereochemistries have been observed. Dipole-moment studies in dilute benzene [1] have shown that the Ti, Sn, Zr, and Hf derivatives of $M(acac)_2X_2$ have a *cis*-configuration and for $Sn(acac)_2Cl_2$ this configuration has been independently assigned from i.r.[2] and n.m.r. studies.[2,3] $Sn(oxine)_2Cl_2$ [4] and $Ti(oxine)_2Cl_2$ [5] also have a *cis*-arrangement but a *trans*-arrangement has been observed for $Re(acac)_2Cl_2$ [6] and $Ti(salen)Cl_2$.[7]

Results of a study [8] of the synthesis and electronic properties of $Mo(chel)_2Cl_2$ complexes were in general accord with those for distorted octahedral structures but it was not possible to assign a *cis*- or *trans*-arrangement. Similar results have been obtained [9] for a series of $Mo(diketone)_2Cl_2$ complexes.

The present crystallographic analysis was undertaken to determine unambiguously the stereochemistry of the molybdenum atom in one of these molybdenum(IV)–chloro-complexes.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{16}Cl_2MoN_2O_2$, $M = 435{\cdot}2$, Monoclinic, $a = 6{\cdot}429 \pm 0{\cdot}006$, $b = 13{\cdot}619 \pm 0{\cdot}014$, $c = 10{\cdot}047 \pm 0{\cdot}010$ Å, $\beta = 107{\cdot}88 \pm 0{\cdot}1°$, $U = 837{\cdot}2$ Å^3, $D_m = 1{\cdot}71$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1{\cdot}73$ g cm^{-3}, $F(000) = 436$ Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 11·00 cm^{-1}. Space group $P2_1/c$ (No. 14, C^5_{2h}) from systematic absences: $h0l$, l odd; $0k0$, k odd.

Unit-cell parameters were obtained by least-squares refinement of the angular settings of 8 accurately centred reflections.

Intensity Measurements.—All intensity data were collected from one crystal of dimensions *ca.* 0·05 × 0·05 × 0·06 mm. Initially, a restricted set of photographic data was collected by use of equi-inclination Weissenberg geometry. A total of 391 independent non-zero reflections were visually estimated from the levels $h0l$, $h1l$, $0kl$, and $1kl$. After cross-correlation and correction for Lorentz polarization effects, these data were sufficient to solve the structure. Subsequently a full data set was collected out to 2θ(Mo-K_α) 60° by use of a Philips PW 1100 diffractometer. These data were collected by the θ—2θ scan technique with a symmetric scan range of ±0·9° in 2θ from the calculated scattering angle and a scan rate of 0·017° s^{-1}. The Mo-K_α radiation was graphite monochromatized, but no reflection was sufficiently strong to require an attenuation filter. Three standard reflections, monitored at two-hourly intervals throughout the data collection, showed no significant variation in intensity.

Intensity data were processed using a program [10] written specifically for the PW 1100 diffractometer. Background-corrected intensities were assigned standard deviations according to: $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where CT is the total integrated peak count obtained in a scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; p was 0·04. The inclusion of this last term prevents unduly high weight being given to strong reflections. The values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects as usual.

Of the 2425 measured reflections, 1325 having $F_o^2 > 2\sigma(F_o^2)$ were used in subsequent calculations.

Neither extinction nor absorption corrections were

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† sal-NR = *N*-substituted salicylaldiminato anion, salen = *NN'*-ethylenebis(salicylaldiminato) anion, acacen = *NN'*-ethylenebis(acetylacetoneiminato) anion.

[1] N. Serpone and R. C. Fay, *Inorg. Chem.*, 1969, **8**, 2379.

[2] J. W. Faller and A. Dovison, *Inorg. Chem.*, 1967, **6**, 182.

[3] J. A. S. Smith and E. J. Wilkins, *Chem. Comm.*, 1965, 381.

[4] I. Douek, M. J. Frazer, Z. Goffer, M. Goldstein, B. Rimmer, and H. A. Willis, *Spectrochim. Acta*, 1967, *A*, **23**, 373.

[5] B. F. Studd and A. G. Swallow, *J. Chem. Soc.* (*A*), 1968, 1961.

[6] C. J. L. Lock and Che'ng Wan, *Chem. Comm.*, 1967, 1109.

[7] G. Gilli, D. W. J. Cruickshank, R. L. Beddoes, and O. S. Mills, *Acta Cryst.*, 1972, *B*, **28**, 1889.

[8] A. van den Bergen, K. S. Murray, and B. O. West, *Austral. J. Chem.*, 1972, **25**, 705.

[9] G. Doyle, *Inorg. Chem.*, 1971, **10**, 2348.

[10] J. Hornstra and B. Stubbe, PW 1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Holland.

applied to these data. For the approximately spherical data crystal, μR is 0·07 and the estimated maximum effect on the intensities caused by the neglect of absorption is $<1\%$.

TABLE 1

Atomic positional and anisotropic thermal parameters,* with estimated standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{13}
Mo	1·0000(0)	0·0000(0)	0·0000(0)	2·90(5)	2·82(5)	3·68(6)	−0·09(7)	1·19(4)	−0·04(7)
Cl	1·2433(4)	0·0699(2)	0·2078(3)	3·76(14)	4·17(14)	3·73(14)	−0·75(12)	0·86(11)	−0·04(12)
O	0·7763(10)	0·0932(4)	0·0134(7)	2·7(4)	3·1(4)	5·0(4)	−0·1(3)	1·6(3)	0·2(3)
N	1·1039(12)	0·1095(5)	−0·1183(8)	2·8(4)	3·0(4)	3·6(5)	−0·3(4)	1·2(4)	0·2(4)
C(1)	0·7728(14)	0·1923(7)	0·0107(10)	2·1(5)	3·4(6)	3·3(5)	0·5(4)	0·2(4)	−0·1(4)
C(2)	0·6305(15)	0·2386(7)	0·0695(10)	3·2(6)	4·2(6)	3·7(6)	0·5(5)	1·1(5)	−0·8(5)
C(3)	0·6203(16)	0·3423(8)	0·0674(11)	4·1(6)	4·1(6)	4·7(7)	0·9(5)	1·5(5)	−0·2(5)
C(4)	0·7450(18)	0·3964(7)	0·0014(11)	5·1(7)	2·9(6)	4·8(7)	0·3(5)	1·2(6)	−0·2(5)
C(5)	0·8844(17)	0·3495(8)	−0·0601(11)	4·8(7)	3·5(6)	5·4(7)	0·6(6)	0·1(6)	−0·4(6)
C(6)	0·9031(16)	0·2452(7)	−0·0542(10)	3·3(5)	2·7(5)	4·0(6)	0·3(5)	−0·6(7)	0·5(5)
C(7)	1·0518(15)	0·2020(7)	−0·1230(10)	3·1(5)	3·6(6)	3·9(6)	−0·4(5)	1·0(5)	−0·5(5)
C(8)	1·2508(16)	0·0813(7)	−0·1982(10)	4·4(6)	4·2(6)	4·2(6)	0·5(5)	3·1(5)	−0·1(5)

* Vibration parameters $\times 10^2$. Atomic scattering factors are expressed as: $f = f_0[\exp - 2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)]$.

Structure Determination and Refinement.—The structure was solved by standard heavy-atom methods using the photographic data. With only two molecules in the unit cell of $P2_1/c$ the molecule must have point-symmetry $\bar{1}$, with the molybdenum atom lying on a centre of inversion. The *trans*-configuration of the molecule was therefore inferred from the space-group data alone as $\bar{1}$ point-symmetry is impossible for the *cis* isomer. The position of the chlorine atom was derived from a three-dimensional Patterson map and two structure-factor calculations, each followed by a difference synthesis, gave the positions of all non-hydrogen atoms.

In the least-squares calculations discussed, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors were taken from ref. 11. A least-squares refinement of the structure with isotropic temperature factors and each reflection given unit weight gave R 0·120 and R' 0·137 {where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}. Refinement was then continued with the full set of diffractometer data and anisotropic thermal parameters for all atoms. This converged after several cycles to give R 0·074 and R' 0·073 but appreciable disagreement was observed for the 252 reflections having $\sin\theta/\lambda \geqslant 0·60$. Many of these reflections were only just over the limit of 2σ and it was considered best to eliminate all 252 reflections from the refinement. Two final cycles of refinement gave a significant improvement with R 0·059 and R' 0·064.

Final values of the positional and vibrational parameters are listed in Table 1, together with their estimated standard deviations derived from the inverse least-squares matrix.

A difference-Fourier map calculated from the final parameters revealed approximate positions for all eight hydrogen atoms in the asymmetric unit. These were idealized assuming C–H 1·05 Å and the approximate trigonal or tetrahedral geometry at the carbon atom. These idealized co-ordinates are given in Table 2. A final structure-factor calculation with all hydrogen atoms included and each given an isotropic temperature factor 1 Å^2 greater than the B value of the associated carbon atom gave R 0·057 and R' 0·059. Observed and calculated structure factors are given in Supplementary Publication No. SUP 20842 (3 pp.).*

Calculations.—All calculations were performed on the Monash University CDC 3200 computer. The major programs used during the refinement were modified versions of ORFLS [12] and the Fourier program of White.[13] All diagrams were drawn by use of the program ORTEP.[14]

TABLE 2

Idealized positional co-ordinates for the hydrogen atoms, numbered according to the carbon atoms to which they are attached

	x/a	y/b	z/c
H(2)	0·532	0·197	0·115
H(3)	0·519	0·379	0·116
H(4)	0·733	0·473	−0·002
H(5)	0·976	0·391	−0·111
H(7)	1·121	0·249	−0·180
H(8a)	1·159	0·050	−0·294
H(8b)	1·333	0·144	−0·217
H(8c)	1·365	0·030	−0·141

DISCUSSION

Figure 1 shows a view of the molecule and defines the labelling scheme for the atoms. The packing arrangement is shown in Figure 2 and Table 3 gives pertinent intramolecular distances and angles together with their estimated standard deviations.

The two chlorine atoms are mutually *trans*, as are the two oxygen and two nitrogen atoms. The Mo–Cl distance [2·388(2) Å] is similar to Mo$^{\text{IV}}$–Cl (2·46 Å) in bis-[1,2-bis(diphenylphosphino)ethane]chloro-oxomolybdenum(IV) trichloro(acetone)zincate,[15] the Re$^{\text{IV}}$–Cl (2·33 Å) in Re(acac)$_2$Cl$_2$,[6] and Ti$^{\text{IV}}$–Cl (2·35 Å) in Ti(salen)Cl$_2$.[7] Bond distances within the salicylaldehyde

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[11] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[12] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS A Fortran Crystallographic Least-Squares Program, Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee, 1962.

[13] J. C. B. White, Melbourne University Fourier Program MUFR 3; see J. S. Rollett, in 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961, p. 87.

[14] C. K. Johnson, ORTEP, Fortran Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee.

[15] V. C. Adam, U. A. Gregory, and B. T. Kilbourn, *Chem. Comm.*, 1970, 1400.

group are in general agreement with mean values reported from a study of several such complexes.[16]

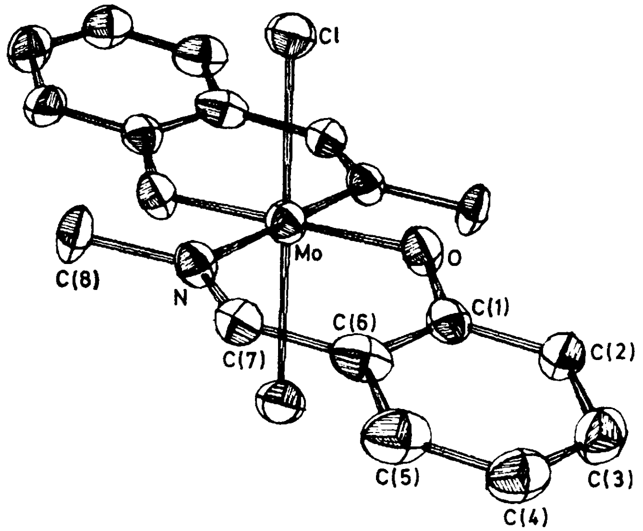

FIGURE 1 A view of the molecule showing the atom labelling system used in the analysis

Mean planes were calculated using the procedure of Blow [17] for the two groups of atoms O,O′,N,N′ and O,N, C(1)—(8) and the plane equations are given in Table 4. The angle between these two planes is 19·0° and the two *N*-methylsalicyaldimine groups are therefore bent in a ‘ symmetric stepped ’ configuration analogous to that adopted by salen in many complexes.[18] This is illustrated in Figure 3 which shows the molecule viewed parallel to a plane fitted through the centroid of the molecule. The Mo–Cl bond is perpendicular to the best plane defined by the atoms O,O′,N, and N′.

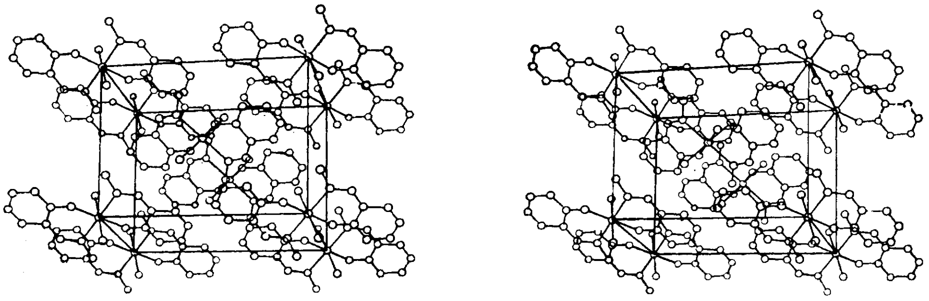

FIGURE 2 Molecular packing of the molecules viewed with *b* vertical and *a** approximately perpendicular to the page. The unit cell is outlined

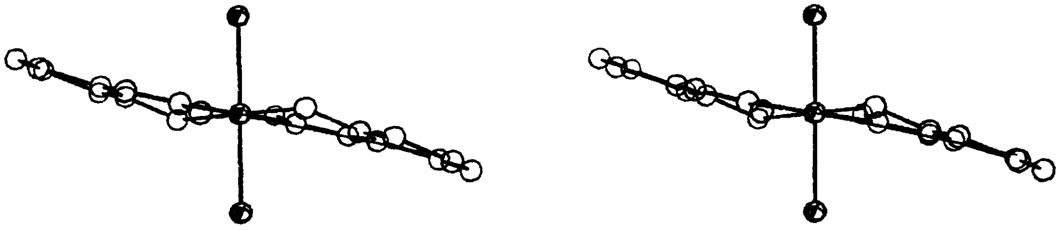

FIGURE 3 The molecule viewed parallel to the mean plane through the Mo atom and the two salicylaldehyde ligands

TABLE 3

Selected intramolecular distances and angles *

(*a*) Distances (Å)

Mo–Cl	2·388(2)	C(2)–C(3)	1·413(14)
Mo–O	1·953(6)	C(3)–C(4)	1·397(17)
Mo–N	2·137(8)	C(4)–C(5)	1·390(17)
N–O	2·819(11)	C(5)–C(6)	1·425(14)
O–C(1)	1·350(11)	C(6)–C(7)	1·464(16)
C(1)–C(2)	1·384(15)	C(7)–N	1·300(12)
C(1)–C(6)	1·407(15)	N–C(8)	1·466(15)

(*b*) Angles (°)

O–Mo–O′	180(0)	C(2)–C(3)–C(4)	120·2(9)
N–Mo–N′	180(0)	C(2)–C(1)–C(6)	122·0(9)
O–Mo–N	87·0(3)	C(3)–C(4)–C(5)	120·7(9)
O–Mo–N′	93·0(3)	C(4)–C(5)–C(6)	119·8(9)
Cl–Mo–O	88·8(2)	C(5)–C(6)–C(1)	118·3(9)
Cl–Mo–N	88·6(2)	C(5)–C(6)–C(7)	116·1(9)
Mo–O–C(1)	131·0(6)	C(6)–C(7)–N	124·8(9)
O–C(1)–C(2)	117·1(8)	C(7)–N–Mo	125·1(7)
O–C(1)–C(6)	120·8(8)	C(7)–N–C(8)	115·8(8)
C(1)–C(2)–C(3)	118·9(9)	C(8)–N–Mo	119·0(6)
C(1)–C(6)–C(7)	125·5(9)		

* Atoms in the same molecule but related by a centre of inversion are indicated by primes.

There are no unusual intermolecular contacts. Excluding hydrogen atoms, the shortest intermolecular contact is 3·40 Å between the oxygen atom of one mole-

TABLE 4

Equations of planes and in square brackets distances of the individual atoms (Å) from the planes. The equations are referred to the orthogonal set of axes *a*, *b*, *c** and *X*, *Y*, and *Z* are co-ordinates in Å

Plane (I): O, N, C(1)—(8)

$$-0{\cdot}4839X - 0{\cdot}0535Y - 0{\cdot}8735Z + 2{\cdot}6143 = 0$$

[O 0·039(6), N −0·088(8), C(1) −0·003(9), C(2) 0·002(10), C(3) −0·027(11), C(4) −0·001(11), C(5) 0·020(11), C(6) −0·002(10), C(7) 0·038(10), C(8) 0·023(10)]

Plane (II): O, N, O′, N′

$$-0{\cdot}3901X - 0{\cdot}3695Y - 0{\cdot}8434Z + 2{\cdot}5078 = 0$$

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[16] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 1966, **88**, 2951.

[17] D. M. Blow, *Acta Cryst.*, 1960, **13**, 168.

cule and the atom C(8^{I}) of an adjacent molecule.* The only atoms within 3·3 Å of each chlorine atom are the the two oxygen and two nitrogen atoms of the same molecule and the six hydrogen atoms (numbered according to the carbon atoms to which they are attached): H(2), H(7^{II}), H(5^{II}), H($8c^{III}$), H(3^{IV}), and H(4^{IV}). The H–Cl distances vary from 2·90 to 3·26 Å, little different from the predicted van der Waals distance (3·0 Å).[19]

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* Roman numerals indicate the following equivalent positions relative to the co-ordinates of Table 1:

I $x - 1, y, z$

II $x - 2, \frac{1}{2} - y, \frac{1}{2} + z$

III $1 - x, -y, -z$

IV $1 - x, y - \frac{3}{2}, \frac{1}{2} - z$

[18] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[19] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, p. 260.