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trans-$[Mo(O)(OH)(dppe)_2]^+$ as its Perchlorate Salt

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Abstract

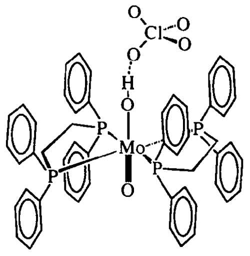
In the perchlorate salt of *trans*-bis[1,2-bis(diphenylphosphino-*P*)ethane](hydroxo)(oxo)molybdenum(IV), *trans*-$[Mo(O)(OH)(dppe)_2]^+$ (dppe = $C_{26}H_{24}P_2$), hydrogen bonding from the hydroxo ligand to the perchlorate counterion prevents the type of disorder often observed in $O\equiv M—X$ units and results in a well defined structure of the cation. The molybdenum–oxo bond length is completely normal for an $Mo^{IV}—O$(oxo) bond. It is argued that the earlier report of the structure of this complex, which has been a source of confusion in the literature, was actually describing disordered *trans*-$[Mo(O)(F)(dppe)_2]BF_4$.

Comment

Low-spin complexes with a d^2 electronic configuration are common among the second and third row transition elements (Nugent & Mayer, 1988). These systems are characterized by having very strong π-donor ligands (O^{2-} and N^{3-}) on the unique axis of a tetragonally compressed octahedron. The coordination sphere is completed by very weak π-donor or even π-acceptor ligands. Some of the most used auxiliary ligands of this type are bidentate phosphines (Dilworth *et al.*, 1983).

Recently, we described the synthesis of orange *trans*-$[Mo(O)(OH)(dppe)_2]ClO_4$ starting from *trans*-$[Mo(O)_2(dppe)_2].2CH_3OH$, which has been structurally characterized (Bendix *et al.*, 1997). An earlier report concerning *trans*-$[Mo(O)(OH)(dppe)_2]BF_4$ (Churchill & Rotella, 1978), but describing it as pink, had led to its classification as an example of bond-stretch isomerism because of the observation of an anomalously long molybdenum–oxo bond (Nugent & Mayer, 1988). However, all the examples of bond-stretch isomerism in metal complexes described so far have been refuted, with this complex as the single exception.

Our method of preparation of the tetrafluoroborate salt often leads to contamination with pink *trans*-$[Mo(O)(F)(dppe)_2]BF_4$ and forcing conditions or prolonged reaction times (days) easily accomplishes complete conversion to the fluoro complex. It is therefore assumed that the earlier report, which described a yield of one single crystal, actually pertains to *trans*-$[Mo(O)(F)(dppe)_2]BF_4$. The origin of the long molybdenum–oxo bond distance in that report lies in the lack of recognition of disorder of the $O\equiv Mo—F$ unit. It was necessary to take such disorder into account in the description (Cotton *et al.*, 1992) of a similar fluoro complex. We report here the crystal structure of *trans*-$[Mo(O)(OH)(dppe)_2]ClO_4$, (I).



(I)

The complex cation has the expected tetragonally compressed octahedral structure and, because of a hydrogen bond between the coordinated hydroxo group and the perchlorate counterion [H1···O6 2.12 (3) Å and O2—H1···O6 167 (3)°], it is not disordered. The bond lengths and angles within the dppe ligands are normal. The molybdenum–phosphorous bond lengths are slightly different but are in the normal range for $Mo^{IV}—P$ bonds (Lorenz *et al.*, 1990). The molybdenum–oxo bond length is 1.7471 (11) Å, which is shorter than the earlier reported bond length of 1.833 (5) Å (Churchill & Rotella,

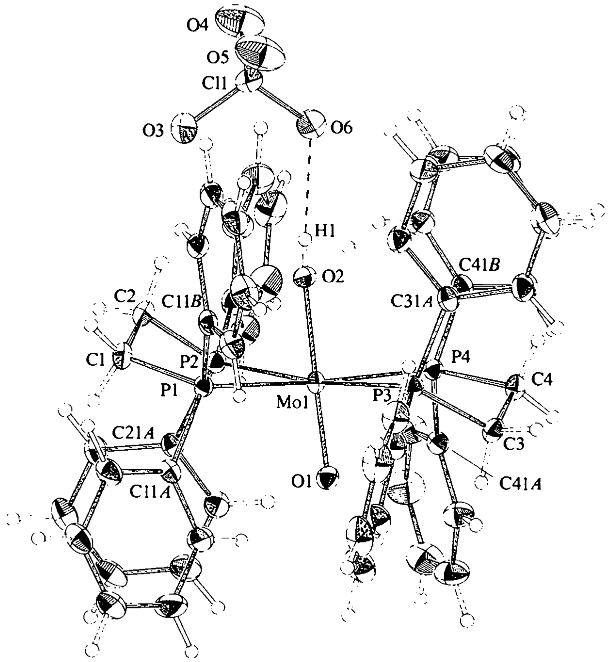


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level; H atoms are shown as spheres of arbitrary size.

1978). The bond length of 1.7471 (11) Å is close to those reported for other molybdenum(IV)–oxo complexes and is in line with the commonly accepted large *trans* influence of oxo ligands, which is reflected in the fact that the bond length is significantly shorter than that of 1.8184 (8) Å found in *trans*-[Mo(O)$_2$(dppe)$_2$].2CH$_3$OH (Bendix *et al.*, 1997). The length of the molybdenum–hydroxo bond is 1.9044 (12) Å, which is not statistically different from the distances found in similar neutral and cationic complexes: 1.922 (8) Å in *trans*-[Mo(OH)(NO)(dppe)$_2$].THF (Kan *et al.*, 1982) and 1.922 (9) Å in *trans*-[Mo(OH)(NH$_2$)(dppe)$_2$](CF$_3$SO$_3$)$_2$ (Adachi *et al.*, 1995). It is, however, significantly shorter than the Mo—OH bond [2.077 (7) Å] in the anion *trans*-[Mo(O)(OH)(CN)$_4$]$^{3-}$ (Robinson *et al.*, 1975).

The Mo—O—H angle of 173 (3)° is larger than normally found for coordinated hydroxo groups. However, a close to linear Mo—O—H group is also found in *trans*-[Mo(OH)(NH$_2$)(dppe)$_2$](CF$_3$SO$_3$)$_2$ (Adachi *et al.*, 1995). The linear ligation of the hydroxo group may, in both cases, be enforced by hydrogen bonding to the counterion, but also electronic synergy between π-accepting equatorial phosphine ligands and axial π donors would favour the linear coordination mode of the hydroxo ligand, in which it is most effective as a π donor.

Experimental

trans-[Mo(O)(OH)(dppe)$_2$]ClO$_4$ was prepared as described previously (Bendix *et al.*, 1997). Crystals suitable for X-ray analysis were obtained by recrystallization from an acetone–water mixture (3:1).

Crystal data

[Mo(O)(OH)(C$_{26}$H$_{24}$P$_2$)$_2$]-ClO$_4$
M_r = 1025.18
Monoclinic
$P2_1/n$
a = 16.825 (4) Å
b = 16.658 (3) Å
c = 17.162 (5) Å
β = 102.18 (2)°
V = 4702 (2) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 19.33–20.55°
μ = 0.523 mm^{-1}
T = 122 (2) K
Irregular
0.40 × 0.25 × 0.25 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
17 693 measured reflections
17 693 independent reflections
14 579 reflections with $I > 2\sigma(I)$

$\theta_{\max}$ = 32.96°
$h = -25 \rightarrow 25$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 26$
5 standard reflections
frequency: 166.7 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.035
17 693 reflections
581 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 4.6914P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.029
$\Delta\rho_{\max}$ = 1.134 e Å^{-3}
$\Delta\rho_{\min}$ = −0.75 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mo1—O1	1.7471 (11)	Mo1—P2	2.5330 (4)
Mo1—O2	1.9044 (12)	Mo1—P4	2.5458 (4)
Mo1—P3	2.5258 (4)	O2—H1	0.70 (3)
Mo1—P1	2.5294 (4)		
O1—Mo1—O2	178.88 (5)	P3—Mo1—P2	173.257 (14)
O1—Mo1—P3	87.50 (4)	P1—Mo1—P2	79.186 (13)
O2—Mo1—P3	93.22 (4)	O1—Mo1—P4	86.29 (4)
O1—Mo1—P1	96.89 (4)	O2—Mo1—P4	93.00 (4)
O2—Mo1—P1	83.86 (4)	P3—Mo1—P4	79.511 (13)
P3—Mo1—P1	98.406 (13)	P1—Mo1—P4	176.153 (13)
O1—Mo1—P2	99.02 (4)	P2—Mo1—P4	102.520 (13)
O2—Mo1—P2	80.29 (4)	Mo1—O2—H1	173 (3)

The hydroxo H atom was found and its coordinates and isotropic displacement parameter were refined. All other H atoms were placed in geometrically calculated positions and allowed to ride on their parent C atom with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The highest difference peak (1.134 e Å^{-3}) was found 0.65 Å from the Mo atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*-97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1040). Services for accessing these data are described at the back of the journal.

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A Polymeric Nickel(II) Thiocyanate Complex of *N*-(2-Aminoethyl)-*N*-methyl-1,2-ethanediamine†

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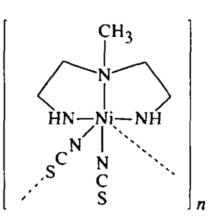
Abstract

The structure of [Ni(medien)(NCS)(μ-SCN)]$_n$ [medien is *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine, $C_5H_{15}N_3$] is a polymeric chain with each pair of neighbouring nickel(II) ions linked by one SCN$^-$ bridging ligand. The coordination polyhedron about the Ni^{II} atom is a distorted octahedron consisting of three N atoms of the medien ligand coordinating facially, one N atom of the non-bridging thiocyanate ligand, and one N and one S atom of two bridging thiocyanate ligands. The five-membered chelate rings display envelope geometry.

Comment

The triamine complexes of nickel(II) thiocyanate exhibit a large variety of molecular structures. Depending on the coordination mode of the SCN$^-$ anion and the chain length of the triamine, the resulting nickel(II) complexes are monomeric (Mukherjee *et al.*, 1994), dimeric (Mondal *et al.*, 1997) or polymeric (Vicente *et al.*, 1994). An X-ray structure analysis of the title complex, [Ni(medien)(NCS)$_2$] [medien is *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine], (I), was motivated by our continued interest in establishing the coordination geometry around the metal centre and the effect of the substituent in the secondary amine on the conformation of the chelate rings.



(I)

The structure of the title complex, (I), is shown in Fig. 1. The structure consists of a polymeric chain of [Ni(medien)(NCS)$_2$] units in a *cis* configuration; each pair of neighbouring nickel(II) ions are linked by one SCN$^-$ bridging ligand. Owing to the presence of one SCN$^-$ terminal ligand on each Ni^{II} atom, the chains are neutral and linked by van der Waals forces in the crystal; there are no hydrogen bonds between the chains. The coordination polyhedron around the metal centre is best described as a distorted octahedron with an N_5S donor set. The two primary N atoms (N3 and N5) of the chelated triamine, the N atom of the non-bridging thiocyanate group (N1) and the symmetry-related S atom of the bridging thiocyanate moiety (S2^{i}; symmetry code as in Table 1) define an equatorial plane around the Ni atom; the remaining two N atoms, N2 and N4, are in *trans*-axial positions, with Ni displaced by 0.089 (1) Å towards N2. Consequently, the title complex has the same structural scheme, [Ni(medien)(NCS)(μ-SCN)]$_n$, as that reported for the μ-thiocyanatonickel(II) compounds (Mondal *et al.*, 1997; Vicente *et al.*, 1994), in which each Ni atom is bridged by only one thio-

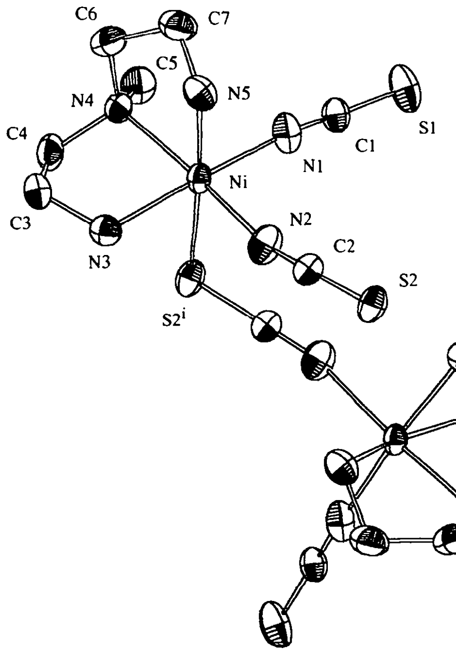


Fig. 1. A view of the title molecule with displacement ellipsoids shown at the 50% probability level.

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† Alternative name: poly[*N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine-κ^3N]-μ-isothiocyanato-*N*:*S*-isothiocyanatonickel(II).