Reactions of Molybdenum Hexacarbonyl with Schiff's Bases

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Reaction of molybdenum hexacarbonyl with potentially tetradentate Schiff's bases gave complexes dicarbonyl-*NN'*-ethylenebis(salicylylaminato)molybdenum(II), (I) [from *NN'*-ethylenebis(salicylideneimine) and also *NN'*-ethylenebis(salicylylamine)], dicarbonylaminobis-*N*-ethylenesalicylylaminato)molybdenum(II) hydrochloride, (II) [from aminobis(*N*-ethylenesalicylideneimine) hydrochloride], and hexacarbonyltris[bis(acetylacetone)ethylenedi-imine]dimolybdenum(0), (III) [from bis(acetylacetone)ethylenedi-imine)]. With 2,2'-bibenzothiazolinyl decomposition of the ligand occurred through abstraction of sulphur by molybdenum. During the reactions which gave complexes (I) and (II) hydrogenation of the C=N bonds of the Schiff's bases occurred. I.r., u.v., and visible spectra and magnetic susceptibilities of the complexes are reported. All three complexes are diamagnetic. Complexes (I) and (II) are considered to be mononuclear, distorted octahedral with *cis*-$(CO)_2$ groups and complex (III) to be binuclear with *cis*-$(CO)_3$ groups, with neutral Schiff's base ligands bound through nitrogen atoms only with one Schiff's base as a bridging ligand. None of the complexes was effective as a catalyst for the reduction of dinitrogen although hydrogenation of the C=N bonds of the Schiff's bases has some similarity to a proposed mechanism of nitrogen fixation.

COMPLEXES of low-valent molybdenum, obtained by reacting molybdenum hexacarbonyl with Schiff's bases, might act as catalysts for the activation and reduction of dinitrogen. In our search for such catalysts, especially with respect to obtaining model systems with the metal in a co-ordination environment similar to that of the metals in nitrogenase, we have concentrated on ligands which provide as donor atoms nitrogen, oxygen, and sulphur. It is well known [1] that Schiff's base complexes of various transition metals interact with small molecules (*e.g.*, dioxygen, nitric oxide) and there has been a report that a manganese(II) Schiff's base complex reacts reversibly with dinitrogen.[2] It is also of interest that tris(*N*-methylsalicylideneiminato)molybdenum(III)

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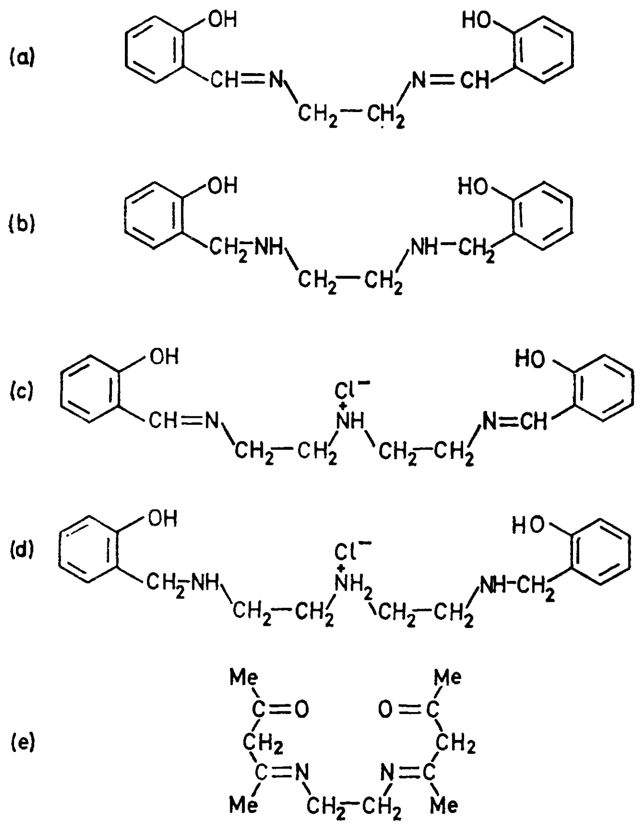
[1] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **8**, 83.

[2] G. L. Johnson and W. D. Beveridge, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 323.

dissolved in toluene absorbs dioxygen[3] and that molybdenum carbonyl halides act as carbon monoxide carriers and interact with other small molecules, *e.g.*, nitric oxide.[4] The structures of the Schiff's bases used in our work and other relevant compounds are given below.



(a) *NN'*-ethylenebis(salicylideneimine), H_2A; (b) *NN'*-ethylenebis(salicylylamine), H_2A'; (c) aminobis(*N*-ethylenesalicylideneimine) hydrochloride, H_2B,HCl; (d) aminobis(*N*-ethylenesalicylylamine) hydrochloride, H_2B',HCl; (e) bis(acetylacetone)ethylenedi-imine, H_2D

EXPERIMENTAL

The following compounds were prepared by established procedures: *NN'*-ethylenebis(salicylideneimine), H_2A,[5a] bis(acetylacetone)ethylenedi-imine, H_2D,[5b] 2,2'-bibenzothiazolinyl, H_2E,[5c] *NN'*-ethylenebis(salicylideneiminato)nickel(II), (IV),[5a] and μ-oxo-bis[*NN'*-ethylenebis(salicylideneiminato)-iron(III)], (V).[5a,6]

Aminobis(N-*ethylenesalicylideneimine*) *Hydrochloride*, H_2B,HCl.—Salicylaldehyde (4·2 ml) was added to diethylenetriamine (2·2 ml) in water (50 ml). To the resulting solution was added 2M-hydrochloric acid, dropwise, until precipitation of the pale yellow compound was complete. The product was dried *in vacuo* over P_2O_5 (Found: C, 62·1; H, 6·3; N, 12·0. $C_{18}H_{21}ClN_3O_2$ requires: C, 62·2; H, 6·3; N, 12·1%).

NN'-*Ethylenebis*(*salicylylamine*), H_2A'.—*NN'*-Ethylenebis(salicylideneimine) (0·7 g) was dissolved in toluene (80 ml). To this solution was added a rhodium–carbon catalyst and the mixture was kept overnight under hydrogen (1500 p.s.i.). The catalyst was removed by filtration, the bulk of the solution was reduced on a rotary evaporator, and light yellow crystals were obtained (Found: C, 70·5; H, 7·5; N, 10·1. $C_{16}H_{20}N_2O_2$ requires: C, 70·6; H, 7·4; N, 10·3%).

The following compounds were prepared by heating molybdenum hexacarbonyl (0·01 mol) and the appropriate Schiff's base (0·01 mol) under reflux in toluene for 12 h [compounds (I) and (II)] and benzene for 3 h [compound (III)]. Solvents were dried by double distillation from sodium wire. All operations were in a closed system under nitrogen. Yields were *ca.* 50%. *Dicarbonyl*-NN'-*ethylenebis*(*salicylylaminato*)*molybdenum*(II), $MoA'(CO)_2$, (I) (Found: C, 51·0; H, 4·2; Mo, 22·7; N, 6·6. $C_{18}H_{18}MoN_2O_4$ requires: C, 51·2; H, 4·3; Mo, 22·7; N, 6·6%). *Dicarbonylaminobis*(N-*ethylenesalicylylaminato*)*molybdenum*(II) *hydrochloride*, $Mo(B',HCl)(CO)_2$, (II) (Found: C, 47·7; H, 4·9; Mo, 18·9; N, 8·4. $C_{20}H_{23}ClMoN_3O_4$ requires: C, 47·9; H, 4·8; Mo, 19·1; N, 8·4%). *Hexacarbonyltris*[*bis*(*acetylacetone*)*ethylenedi-imine*]*dimolybdenum*(0), $Mo_2(H_2D)_3(CO)_6$, (III) (Found: C, 48·6; H, 5·9; Mo, 19·0; N, 7·9. $C_{21}H_{30}MoN_3O_6$ requires: C, 48·8; H, 5·8; Mo, 18·6; N, 8·1%). The complexes (I)—(III) were dark brown solids, insoluble in water and organic solvents, which decomposed slowly (*ca.* 1 day) in air with loss of carbon monoxide.

Black products were obtained from molybdenum hexacarbonyl with 2,2'-bibenzothiazolinyl for which analytical data did not correspond with any definite composition. S : N ratios were >1 indicating that abstraction of sulphur from the ligand had occurred (*cf.* ref. 7).

Physical Measurements.—U.v. and visible diffuse reflectance spectra were measured with a Unicam SP 700 spectrophotometer against magnesium oxide. I.r. spectra were measured with a Unicam SP 200 spectrophotometer for the compounds in Nujol mulls or potassium bromide discs. Magnetic susceptibilities were measured on powdered samples with a Newport Instruments Ltd. Gouy balance system calibrated with cobalt mercury thiocyanate.

Analyses.—Molybdenum was determined gravimetrically as the 8-hydroxyquinolinate, $MoO_2(C_9H_6NO)_2$, after decomposing the complexes with a 1 : 1 mixture of perchloric and sulphuric acids. Carbon, hydrogen, nitrogen, and sulphur were determined by standard microanalytical techniques.

RESULTS AND DISCUSSION

We obtained identical products from the reactions of molybdenum hexacarbonyl with the Schiff's base *NN'*-ethylenebis(salicylideneimine) and the hydrogenated base *NN'*-ethylenebis(salicylylamine). Presumably hydrogen required for the hydrogenation is provided through reduction by zerovalent molybdenum of the protons released when the -OH groups of the Schiff's

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[3] F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc.* (*A*), 1969, 1378.

[4] R. Colton and C. J. Rix, *Austral. J. Chem.*, 1970, **23**, 441.

[5] (*a*) P. Pfeiffer, E. Breith, E. Lubbe, and T. Tsumaki, *Annalen*, 1933, **503**, 84; (*b*) A. E. Martell, R. L. Belford, and N. Calvin, *J. Inorg. Nuclear Chem.*, 1958, **5**, 170; (*c*) H. Jadamus, Q. Fernando, and H. Freiser, *J. Amer. Chem. Soc.*, 1964, **86**, 3056.

[6] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1967, 1014.

[7] A. Butcher, Ph.D. Thesis, Reading, 1968.

base react with the metal (*cf.* the reactions of molybdenum hexacarbonyl with acetic acid[8] and acetylacetone[9]).

I.r. Spectra.—Structurally diagnostic bands are listed in the Table. (a) *CO Stretching wavenumbers.* The dicarbonyl complexes (I) and (II) and complex (III) had strong bands in the region 1890—1895 and 1740—1760 cm^{-1}. There were no bands of the organic ligands in these regions so we assign the bands to CO stretching vibrations. The bands are in the region found for terminal carbon monoxide in molybdenum carbonyls substituted with strong σ-donor ligands without π-acceptor ability [*cf.* (dien)Mo(CO)$_3$ and Mo$_2$(CO)$_6$(en)$_3$ in the Table].[10] The structures which give rise to two CO stretching vibrations are for complexes (I) and (II) *cis*-Mo(CO)$_2$ and for complex (III) *cis*-Mo(CO)$_3$.[10] Some samples of complex (I) prepared from the Schiff's base, but not samples prepared from the hydrogenated Schiff's base, had an i.r. band at 1853 cm^{-1} which could arise from *trans*-(CO)$_2$.

Infrared spectra *

	Band maxima and assignments [a]			
Compound †	ν(OH)	ν(NH)	ν(CO)	ν(C=N)
H_2A	2670ms 2590ms			1550w
Mo(A′)(CO)$_2$, (I)		3265m	1895s 1762s (1853s)	
H_2B,HCl	2590s 2455s	2780sh		1530w
Mo(B′HCl)(CO)$_2$, (II)		3100ms 2770sh	1890s 1754s	
H_2D	3150m 1612s			1524s
Mo$_2$(CO)$_6$(H$_2$D)$_3$, (III)	3100m 1612s		1888s 1740s	1530s
Ni(A)				1538s
(FeA)$_2$O				1545s
Mo(CO)$_2$(phen)$_2$ [b]			1784s 1724s	
Mo(CO)$_3$(NH$_3$)$_3$ [c]			1880s 1730s	
Mo(CO)$_3$(dien) [d]			1883s 1723s	
Mo$_2$(CO)$_6$(en)$_3$ [e]			1881s 1730s	

* For compounds in Nujol mulls and KBr discs. Positions of band maxima in cm^{-1}. † For Schiff's bases see text, p. 1829. dien, diethylenetriamine; phen, 1,10-phenanthroline; en, ethylenediamine.

[a] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, London, 1963; L. J. Bellamy, 'Infrared Spectra of Complex Molecules,' Methuen, London, 1958. [b] B. Hutchinson and K. Nakamoto, *Inorg. Chim. Acta*, 1969, **3**, 591. [c] C. G. Barlow and G. C. Holywell, *J. Organometallic Chem.*, 1969, **16**, 439. [d] E. W. Abel, M. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 2323. [e] H. Werner and R. Prinz, *Chem. Ber.*, 1967, **100**, 265.

(b) *Organic ligands.* (i) OH *Stretching vibrations.* In the spectra of the unco-ordinated Schiff's bases H_2A and H_2B,HCl and the hydrogenated base H_2A' (see the Table) there are bands in the range *ca.* 2500—2700 cm^{-1} which we assign to stretching vibrations of OH groups involved in hydrogen bonding. These bands are not present in the spectra of complexes (I) and (II) and so the dianions are bonded to the metal. In the spectra of both the Schiff's base H_2D and its molybdenum complex (III) there are bands at *ca.* 3100 cm^{-1} assigned to OH stretching vibrations and also strong bands at 1612 and 1290 cm^{-1} assigned to vibrations of OH in hydrogen bonded rings. Thus the –OH groups of the base are not bonded to molybdenum in complex (III).

(ii) NH *Vibrations.* We assign bands at *ca.* 3100—3300 cm^{-1} in the spectra of the hydrogenated base H_2A' and complexes (I) and (II) to NH vibrations. In the spectra of the Schiff's base H_2B,HCl and in its molybdenum complex (III) there is a strong band at *ca.* 2780 cm^{-1} which we assign to NH stretching vibrations of the $-NH_2^+$ group. Thus the base H_2B co-ordinates as its hydrochloride and is presumably tetradentate.

(iii) C=N *Vibrations.* Stretching vibrations of the C=N groups of the unco-ordinated Schiff's bases give weak bands at *ca.* 1550 cm^{-1} which are much stronger in the spectra of the co-ordinated bases [*cf.* the nickel complex, (IV), the iron complex, (V), and the molybdenum complex, (III)]. In complexes (I) and (II) C=N stretching vibrations are absent.

Electronic Spectra.—In the spectra of complexes (I)—(III) an intense absorption band extended through the u.v. and visible regions from 40,000 to 15,000 cm^{-1}. Because of the intense absorption in the visible region it was not possible to observe *d–d* transitions.

Structures.—(*a*) *Dicarbonyl complexes* (I) *and* (II). The organic ligands in both complexes are the anions of the hydrogenated Schiff's bases (analytical and i.r. data) and the CO-groups are terminal with the *cis*-configuration (i.r. spectra). A third CO-band in some samples of complex (I) suggests the presence of some *trans*-isomer. The low magnetic moments ($<0{\cdot}5\mu_B$ at 293 K) of the complexes [compared with expected values for octahedral mononuclear molybdenum(II) of *ca.* $2{\cdot}8\mu_B$[11]] could be due to Mo–Mo interaction in a bi- or poly-nuclear structure [*cf.* molybdenum(II) acetate[12]] or, for a mononuclear complex, to splitting of the t_{2g} orbitals such that four *d*-electrons are paired in a low energy doublet as a consequence of the effects of distortion from octahedral symmetry due to different ligands and π-bonding involving only carbon monoxide. In terms of the general pattern of substitution reactions of molybdenum hexacarbonyl, formation of mononuclear substituted dicarbonyl complexes seems most likely. It is also relevant that reaction of *N*-methylsalicylideneimine with molybdenum hexacarbonyl yields a mononuclear molybdenum(III) complex.[3] We suggest that complex (I) is a mixture of isomers (a) and (b) below and that complex (II) has a structure corresponding to the *cis*-isomer (a).

(b) *Complex* (III), Mo$_2$(CO)$_6$(H$_2$D)$_3$. The organic

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[8] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 1964, 2538.

[9] T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 263.

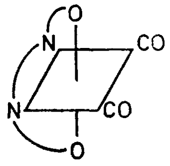
[10] E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1969, **23**, 325.

[11] P. C. H. Mitchell, *Co-ordination Chem. Rev.*, 1966, **1**, 315.

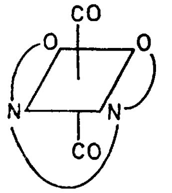
[12] D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

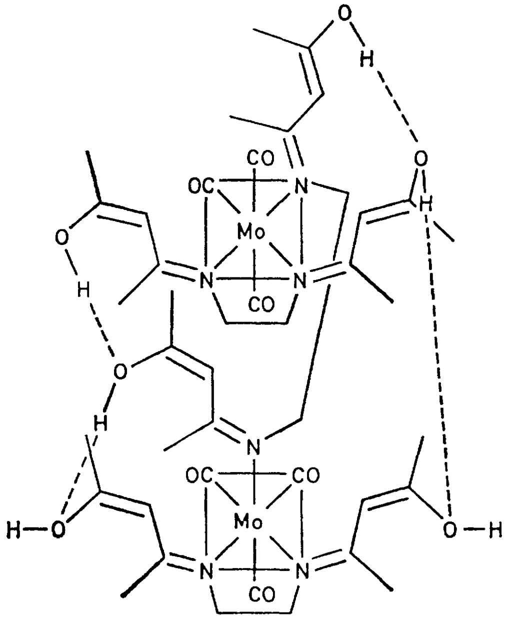
ligand is the neutral Schiff's base bidentate through nitrogen (analytical and i.r. data). CO Stretching wavenumbers of co-ordinated carbon monoxide are close to the values observed for mononuclear substituted molybdenum carbonyl complexes with three mutually *cis*-CO groups [*e.g.*, (dien)$Mo(CO)_3$,[13] $(NH_3)_3Mo(CO)_3$] [14] and $Mo_2(CO)_6(en)_3$.[15] The structure of the last complex is not known but is presumably the same as that of our complex (III). We suggest that bridging occurs *via* the organic ligands giving structure (c) below. With reasonable bond lengths and angles we were able to construct a model of this structure. A feature of interest is the possibility of intramolecular hydrogen bonding involving the ‒OH groups of all three Schiff's bases. Similar bridging by a bidentate ligand has been suggested in the complexes $Mo_2X_4(CO)_4(dpe)_3$ [where X is Cl, Br, or I; dpe is bis(diphenylphosphino)ethane].[16]

(a)



(b)





(c)

Reactions.—Formation of complexes (I) and (II) involves hydrogenation of the C=N bonds of the Schiff's bases. Hydrogenation of the free bases requires a powerful reducing agent, *e.g.*, sodium borohydride or hydrogen under pressure and a catalyst. Evidently co-ordination of the Schiff's bases to zero- or low-valent molybdenum activates the C=N bond towards hydrogenation. In the complexes the orientation of co-ordinated ‒OH and ‒C=N groups is such that direct transfer of hydrogen from oxygen to carbon or nitrogen is possible. It is interesting that hydrogenation of the C=N bond has some similarities to a mechanism proposed for the reduction of co-ordinated dinitrogen, *i.e.* transfer of hydrogen from a co-ordinated ‒OH group to dinitrogen.[17] A consequence of hydrogenation of the C=N bonds is that rotation about the CN bond becomes possible giving the *cis*-structure [(a) above]; evidently this is the preferred structure. In samples of complex (I) prepared from the Schiff's base there was evidence for the presence of some *trans*-isomer but not for samples of complex (I) prepared from the hydrogenated Schiff's base or in samples of complex (II). For these bases there is no steric requirement of planarity on co-ordination. Thus it appears that the initial reaction of a Schiff's base with molybdenum hexacarbonyl may give a planar Schiff's base complex which, after hydrogenation of the C=N bonds, isomerises to the *cis*-structure.

Reaction of molybdenum hexacarbonyl with the Schiff's base bis(acetylacetone)ethylenedi-imine to give complex (III) is not accompanied by hydrogenation. It appears that this base is co-ordinated only through nitrogen and that the ‒OH groups (assuming the enol form) do not react. Instead the ‒OH groups become involved in a network of hydrogen bonds.

Attempted Catalysis of Nitrogen Fixation.—Suspensions of the complexes in ethanol were exposed to mixtures of nitrogen and hydrogen gases (1 : 3 by volume) at atmospheric pressure and 1500 p.s.i. for 16 h. The outlet gas was tested for ammonia by an electrochemical method.[18] The contents of the reaction vessels were boiled with concentrated sodium hydroxide solution and any gaseous products were tested for ammonia. All tests for ammonia were negative.

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[15] H. Werner and R. Prinz, *Chem. Ber.*, 1967, **100**, 265.

[16] M. W. Anker, R. Colton, C. J. Rix, and I. B. Tomkins, *Austral. J. Chem.*, 1969, **22**, 1341.

[17] A. Shilov, N. Denisov, O. Efimov, N. Shuvalov, N. Shuvalova, and A. Shilova, *Nature*, 1971, **231**, 460.

[18] N. S. Segal and R. Wodley-Smith, *Analyt. Chem.*, 1966, **38**, 828.