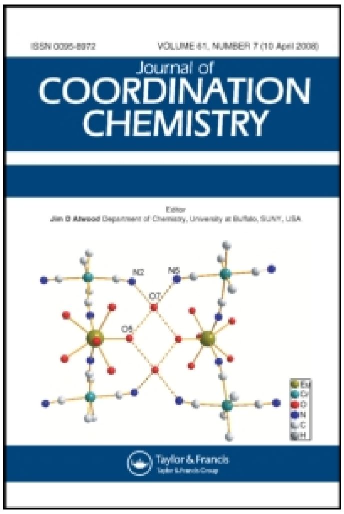

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SEVEN-COORDINATE THIOSEMICARBAZIDE AND THIOSEMICARBAZONE COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

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The complexes $[MI_2(CO)_3(NCMe)_2]$(M = Mo or W) react with an equimolar quantity of thiosemicarbazide ($NH_2NHCSNH_2$; $\overset{\frown}{NS}$) or the thiosemicarbazones $RR'CNNHCSNH_2$ (R = R' = Me or Et; R = Me, R' = ^{i}Pr; R = Ph, R' = H; $\overset{\frown}{NS}$) in methanol at room temperature to give dinuclear iodide-bridged molybdenum compounds $[Mo(\mu-I)I(CO)_2(\overset{\frown}{NS})]_2$ or mononuclear tungsten complexes $[WI_2(CO)_3(\overset{\frown}{NS})]$.

Keywords: Molybdenum, tungsten, thiosemicarbazide, thiosemicarbazones, seven-coordination

INTRODUCTION

Thiosemicarbazide ($NH_2NHCSNH_2$) and thiosemicarbazones ($RR'CNNHCSNH_2$) are generally coordinated to a transition metal centre *via* the sulfur and nitrogen atoms as shown in Figure 1. Although a wide variety of 'classical' transition metal complexes containing thiosemicarbazide and thiosemicarbazones has been reported,[1,2] it is only recently that organo-transition metal compounds containing these ligands have been prepared.[3-6] In this paper we wish to describe the preparation of the first examples of seven-coordinate complexes of molybdenum(II) and tungsten(II) containing thiosemicarbazide and thiosemicarbazones as ligands.

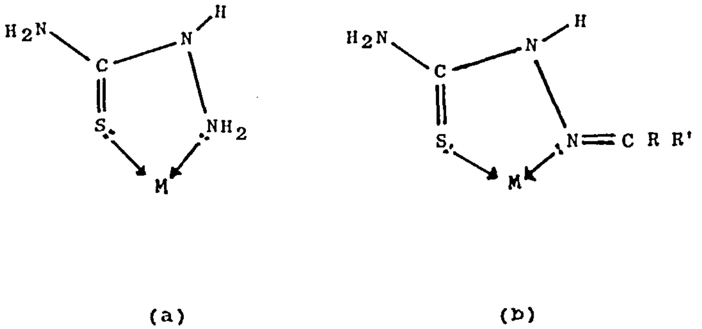

FIGURE 1 Thiosemicarbazide (a) and thiosemicarbazones (b) attached as bidentate ligands to a transition-metal centre.

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EXPERIMENTAL

All reactions described in this paper were carried out under a nitrogen atmosphere using standard Schlenk line techniques. The compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared according to the literature method,[7] and the thiosemicarbazones $(RR'CNNHCSNH_2)$(R = R' = Me or Et; R = Me, R' = ^iPr; R = Ph, R' = H) were synthesized by the method of Sah and Daniels.[8] All other chemicals were purchased from commercial sources.

Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Carlo-Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded either on a Perkin-Elmer 197 or a 1430 infrared spectrophotometer. The molecular weights of $[Mo(\mu\text{-}I)I(CO)_2(R_2CNNHCSNH_2)]_2$ (R = Me or Et) were determined by Rast's method[9] using camphor as solvent. Magnetic susceptibilities were measured using a Johnson-Matthey magnetic susceptibility balance.

$[Mo(\mu\text{-}I)I(CO)_2(NH_2NHCSNH_2)]_2$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.204 g, 0.395 mmol) dissolved in methanol (15 cm^3) with continuous stirring under a stream of nitrogen was added $NH_2NHCSNH_2$ (0.036 g, 0.395 mmol). After stirring the solution for 3 min, filtration and removal of solvent *in vacuo* gave black crystals of $[Mo(\mu\text{-}I)I(CO)_2(NH_2NHCSNH_2)]_2$ (yield = 0.138 g, 70%), which were recrystallized from methanol.

Similar reactions of $[MoI_2(CO)_3(NCMe)_2]$ with $N\frown S$ = $RR'CNNHCSNH_2$ (R = R' = Me or Et; R = Me, R' = ^iPr, R = Ph, R' = H) gave the complexes $[Mo(\mu\text{-}I)I(CO)_2(N\frown S)]_2$(2–5). Reaction times for $2[MoI_2(CO)_3(NCMe)_2] + 2N\frown S \rightarrow [Mo(\mu\text{-}I)I(CO)_2(N\frown S)]_2 + 4NCMe + 2CO$ at 25°C were (2) $N\frown S = Me_2CNNHCSNH_2$, 5 min; (3) $N\frown S = Et_2CNNHCSNH_2$, 20 min; (4) $N\frown S = Me^iPrCNNHCSNH_2$, 5 min; (5) $N\frown S = PhHCNNHCSNH_2$, 5 min.

Molecular weight determined for $[Mo(\mu\text{-}I)I(CO)_2(Me_2CNNHCSNH_2)]_2$ (2): found, 1080; calcd. 1074. Molecular weight determined for $[Mo(\mu\text{-}I)I(CO)_2(Et_2CNNHCSNH_2)]_2$ (3); found, 1090; calcd. 1130.

$[WI_2(CO)_3(PhHCNNHCSNH_2)]$ (10)

To $[WI_2(CO)_3(NCMe)_2]$(0.205 g, 0.340 mmol) dissolved in methanol (15 cm^3) with continuous stirring under a stream of nitrogen was added $PhHCNNHCSNH_2$ (0.061 g, 0.340 mmol). After stirring the solution for 30 min, filtration and removal of solvent *in vacuo* gave brown crystals of $[WI_2(CO)_3(PhHCNNHCSNH_2)]$ (10) (yield = 0.176 g, 74%), which were recrystallized from methanol.

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with $N\frown S = NH_2NHCSNH_2$ or $RR'CNNHCSNH_2$ (R = R' = Me or Et; R = Me, R' = ^iPr) gave the complexes $[WI_2(CO)_3(N\frown S)]$ (6–9). Reaction times for $[WI_2(CO)_3(NCMe)_2] + N\frown S$ – $[WI_2(CO)_3(N\frown S)] + 2NCMe$ at +25°C were (6) $N\frown S = NH_2NHCSNH_2$, 5 min; (7) $N\frown S = Me_2CNNHCSNH_2$, 30 min; (8) $N\frown S = Et_2CNNHCSNH_2$, 5 min; (9) $N\frown S = Me^iPrCNNHCSNH_2$, 5 min.

TABLE I

Analytical data for the complexes $[Mo(\mu\text{-}I)I(CO)_2(\overset{\frown}{N\,S})]_2$ and $[WI_2(CO)_3(\overset{\frown}{N\,S})]$.

Complex	Colour	Yield(%)	Found % (Calcd. %) C	H	N
(1) $[Mo(\mu\text{-}I)I(CO)_2(NH_2NHCSNH_2)]_2$	Black	70	7.2 (7.0)	1.2 (1.0)	8.0 (8.2)
(2) $[Mo(\mu\text{-}I)I(CO)_2(Me_2CNNHCSNH_2)]_2$	Black	70	12.9 (13.0)	1.8 (1.6)	7.4 (7.6)
(3) $[Mo(\mu\text{-}I)I(CO)_2(Et_2CNNHCSNH_2)]_2$	Black	73	15.3 (16.5)	2.4 (2.3)	7.1 (7.2)
(4) $[Mo(\mu\text{-}I)I(CO)_2(Me^iPrCNNHCSNH_2)]_2$	Black	72	15.6 (16.5)	2.6 (2.3)	6.8 (7.2)
(5) $[Mo(\mu\text{-}I)I(CO)_2(PhHCNNHCSNH_2)]_2$	Black	71	19.8 (20.0)	1.8 (1.5)	6.6 (7.0)
(6) $[WI_2(CO)_3(NH_2NHCSNH_2)]$	Brown	84	7.8 (7.8)	1.0 (0.8)	6.9 (7.0)
(7) $[WI_2(CO)_3(Me_2CNNHCSNH_2)]$	Brown	71	13.0 (12.9)	1.7 (1.4)	6.3 (6.5)
(8) $[WI_2(CO)_3(Et_2CNNHCSNH_2)]$	Brown	39	15.8 (15.9)	2.2 (1.9)	6.4 (6.2)
(9) $[WI_2(CO)_3(Me^iPrCNNHCSNH_2)]$	Brown	32	15.7 (15.9)	2.1 (1.9)	6.0 (6.2)
(10) $[WI_2(CO)_3(PhHCNNHCSNH_2)]$	Brown	74	18.3 (18.8)	1.5 (1.3)	5.9 (6.0)

TABLE II

I.r.[a] data for the complexes $[\mathrm{Mo}(\mu\text{-I})\mathrm{I(CO)_2}(\overset{\frown}{\mathrm{N\,S}})]_2$ and $[\mathrm{WI_2(CO)_3}(\overset{\frown}{\mathrm{N\,S}})]$.

Complex	v(CO)cm^{-1}	v(NH$_2$)/cm^{-1}	v(CS)/cm^{-1}
(1)	2080 (s), 2035 (s) and 1955 (br)	1632 (s) and 1553 (m)	692 (w)
(2)	2070 (m), 2015 (s) and 1935 (s)	1630 (m) and 1568 (m)	730 (w)
(3)	2080 (s), 2020 (s), 1943 (m) and 1873 (w)	1616 (m) and 1552 (m)	735 (w)
(4)	2075 (s), 2040 (s) and 1940 (s)	1620 (m) and 1565 (m)	743 (w)
(5)	2070 (s), 2020 (s) and 1944 (s)	1605 (m) and 1555 (m)	755 (w)
(6)	2075 (m), 2040 (s), 2000 (m) and 1942 (s)	1650 (m)	
(7)	2070 (m), 2030 (s), 1940 (s) and 1912 (sh)	1608 (s) and 1560 (m)	755 (w)
(8)	2070 (s), 2015 (s) and 1931 (s)	1609 (m) and 1535 (m)	735 (w)
(9)	2070 (s), 2035 (s), 1995 (s) and 1930 (s)	1614 (m) and 1545 (m)	740 (w)
(10)	2065 (w), 2030 (m), 2000 (m) and 1930 (s)	1605 (m) and 1562 (m)	757 (w)

[a] Spectra recorded as thin films in CH_3OH between NaCl plates; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

RESULTS AND DISCUSSION

The starting materials for this research are the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)[7] which are prepared by reacting the zero-valent trisacetonitrile compounds $[M(CO)_3(NCMe)_3]$[10] *in situ* with one equivalent of I_2 to give quantitative yields of the seven-coordinate complexes. Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and $NH_2NHCSNH_2(N^\frown S)$ or $RR'CNNHCSNH_2$ ($R = R' =$ Me or Et; R = Me, R' = ^{i}Pr; R = Ph, R' = H) $(N^\frown S)$ react in methanol at room temperature to give either the dimeric molybedenum complexes $[Mo(\mu\text{-}I)I(CO)_2(N^\frown S)]_2$ (1–5) or the mononuclear tungsten compounds $[WI_2(CO)_3(N^\frown S)]$ (6–10) in good yield. All the new seven-coordinate complexes (1–10) described in this paper were characterized by elemental analysis (C, H and N; Table I) and i.r. spectroscopy (Table II). The dimeric nature of the complexes $[Mo(\mu\text{-}I)I(CO)_2(RR'CNNHCSNH_2)]_2$ (R = R' = Me or Et) was confirmed by molecular weight studies using Rast's method[9] (see Experimental). Magnetic susceptibility measurements have shown the complexes (1–10) to be diamagnetic as expected since they obey the effective atomic number rule. The complexes (1–10) are very air-sensitive in solution and sensitive to air in the solid state, although the solids may be stored under nitrogen at 0°C for short periods of time. The complexes are not very soluble in chlorinated solvents, particularly the thiosemicarbazide compounds, but are much more soluble in methanol.

Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of the ligands $NH_2NHCSNH_2(N^\frown S)$ and $RR'CNNHCSNH_2(N^\frown S)$ must initially afford the seven-coordinate monomers $[MI_2(CO)_3(N^\frown S)]$ *via* substitution of the two labile acetonitrile ligands. Acetonitrile is mainly a σ-donor ligand and is usually weakly coordinated to an organo-transition metal centre. The molybdenum complexes $[MoI_2(CO)_3(N^\frown S)]$ rapidly lose carbon monoxide to give the iodide-bridged dimers $[Mo(\mu\text{-}I)I(CO)_2(N^\frown S)]_2$ (1–5) which were isolated and characterized. The dimerization of molybdenum complexes of the type $[MoX_2(CO)_3L_2]$ to give $[Mo(\mu\text{-}X)X(CO)_2L_2]_2$ has been previously observed by Moss and Shaw.[11] The ease of dimerization of the molybdenum compounds $[MoI_2(CO)_3(N^\frown S)]$ as compared to the tungsten analogues may be due to the slightly smaller size of molybdenum(II). The i.r. spectral properties {ν(CO)} of the monomeric complexes $[WI_2(CO)_3(N^\frown S)]$ (6–10) are similar to other seven-coordinate complexes of the type $[MX_2(CO)_3(L^\frown L)]$ (M = Mo or W; X = Cl, Br or I; $L^\frown L$ = bidentate ligand).[12–16] Since the X-ray crystal structures of seven-coordinate complexes of the type $[MX_2(CO)_3(L^\frown L)]$ usually have capped octahedral or distorted capped octahedral geometry,[12–16] it is likely that the compounds $[WI_2(CO)_3(N^\frown S)]$ (6–10) have this geometry. The structure of the bromide-bridged dimer $[W(\mu\text{-}Br)Br(CO)_4]_2$ has been determined by Cotton and co-workers[17] and shows that each tungsten centre is in a capped octahedral environment. Since the molybdenum complexes $[Mo(\mu\text{-}I)I(CO)_2(N^\frown S)]_2$ (1–5) are analogous to the tungsten compound $[W(\mu\text{-}Br)Br(CO)_4]_2$, they are likely to have a similar geometry.

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REFERENCES

1. M.J.M. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975).
2. S. Padhye and G.B. Kauffman, *Coord. Chem. Rev.*, **63**, 127 (1985).
3. P.K. Baker, M.J.M. Campbell and M.V. White, *Inorg. Chim. Acta*, **98**, L27 (1985).
4. M.J.M. Campbell, E. Houghton, V. Rogers and P.K. Baker, *Synth. React. Inorg. Met-Org. Chem.*, **16**, 1237 (1986).
5. V. Srivastava, S. Sengupta and S.C. Tripathi, *Synth. React. Inorg. Met-Org. Chem.*, **15**, 163 (1985).
6. M.J.M. Campbell, E. Morrison, V. Rogers and P.K. Baker, *Transition Met. Chem.*, **11**, 381 (1986).
7. P.K. Baker, S.G. Fraser and E.M. Keys, *J. Organomet. Chem.*, **309**, 319 (1986).
8. P.P.T. Sah and T.C. Daniels, *Recueil*, **69**, 1545 (1950).
9. F.G. Mann and B.C. Saunders, *"Practical Organic Chemistry"*, (Longman's Green and Co. Ltd., 1954), pp. 342–344.
10. D.P. Tate, W.R. Knipple and J.M. Augl, *Inorg. Chem.*, **1**, 433 (1962).
11. J.R. Moss and B.L. Shaw, *J. Chem. Soc. (A)*, 595 (1970).
12. M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, 1329 (1972).
13. M.G.B. Drew and C.J. Rix, *J. Organomet. Chem.*, **102**, 467 (1975).
14. A. Mercer and J. Trotter, *Can. J. Chem.*, **52**, 3331 (1974).
15. J.C. Dewan, K. Henrick, D.L. Keppert, K.R. Trigwell, A.H. White and S.B. Wild, *J. Chem. Soc., Dalton Trans.*, 546 (1975).
16. M.G.B. Drew and A.P. Wolters, *Acta Cryst.*, **B33**, 205 (1977).
17. F.A. Cotton, L.R. Falvello and J.H. Meadows, *Inorg. Chem.*, **24**, 514 (1985).