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Transition Metal–Dithiolene Complexes. XI.[1] *cis*-Dinitrosylbis(dithiolene) and Related Complexes of Molybdenum and Tungsten

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Received June 27, 1969

The syntheses of *cis*-dinitrosylbis(1,2-dithiolene) complexes of molybdenum and tungsten, $M(NO)_2S_4C_4(CN)_4^{2-}$ and $M(NO)_2(S_2C_6Cl_4)_2^{2-}$ (M = Mo or W), and of the related bis(1,1-dicyanoethylene-2,2-dithiolates), $M(NO)_2(S_2C{=}C(CN)_2)_2^{2-}$, are described. The complexes have been investigated by voltammetry, and electrochemical and ir and esr spectral evidence for monoanionic species is presented.

In a continuation of our investigations of transition metal–dithiolene complexes, we have studied the reactions between $Mo(NO)_2Cl_2Br_2^{2-}$ and its tungsten analog and $S_2C_2(CN)_2^{2-}$, $S_2C_6Cl_4^{2-}$, $S_2C_6H_3CH_3^{2-}$, and $S_2C{=}C(CN)_2^{2-}$. These reactions provide complexes of the type $M(NO)_2\text{–}(S\text{–}S)_2^{z}$,[3] where z is normally -2, and the complexes are formally isoelectronic with the known bis(dithiocarbamates) $M(NO)_2(S_2CNR_2)_2$.[4] Our original intention in carrying out this work was to compare the relative π-acceptor properties of the *cis*-1,2-dithiolato ligands with the dithiocarbamates, particularly when the metal was in a low formal oxidation state, using as a probe the relative positions of the NO stretching frequencies. A comparable study has been made of tetracarbonylmanganese–dithiolato systems,[5] and a preliminary report of our results obtained from the nitrosyldicyanodithiolene species has been presented.[6] Our earlier work has now been extended by a voltammetric examination of the new dinitrosyl complexes.

Experimental Section

Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate, $Na_2S_2C_2(CN)_2$,[7] tetrachlorobenzene-1,2-dithiol,[8] and disodium 1,1-dicyanoethylene-2,2-dithiolate[9] were prepared by published methods as were $[M(NO)_2Cl_2]_n$ complexes (M = Mo or W).[10] Toluene-3,4-dithiol was purchased from Eastman Kodak, and $[(C_6H_5)_4P]Br$ was prepared by a modification of the method of Chatt and Mann.[11]

Conductivity measurements were determined at room temperature (20°) using a Philips conductivity meter. Esr spectra were obtained in solution at room temperature using a Varian V-4500 X-band spectrometer. Electronic and infrared spectra were recorded with Unicam SP700 and SP100 and Infracord 457 spectrophotometers.

Voltammetric data were obtained using a Heathkit Model EUW-401 polarograph with a platinum electrode rotating at 620 rpm. Dichloromethane was employed as the solvent and $[(C_2H_5)_4N][ClO_4]$ as the base electrolyte. All measurements were standardized against a saturated calomel electrode containing 1 M aqueous LiCl.

All melting points are uncorrected, and elemental analyses were determined by the microanalytical laboratory of this department.

$[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$.—NOCl gas was passed through a well-stirred supension of $Mo(CO)_6$ (2.64 g) in degassed dichloromethane (100 ml). After several minutes, a vigorous reaction took place, CO gas was copiously evolved, and a green solid was deposited. After standing for 1 hr, the solvent was removed *in vacuo* leaving the green $[Mo(NO)_2Cl_2]_n$. The solid was then dissolved under nitrogen in degassed ethanol (40 ml) and to the green solution was added $[(C_6H_5)_4P]Br$ (8.2 g) dissolved in degassed ethanol (150 ml). The volume of the solution was then reduced *in vacuo* to 25 ml and ether was added until precipitation began. On standing at 0° for *ca.* 1 hr, the yellow-green precipitate was filtered off and recrystallized from dichloromethane–ether giving 10.2 g of $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$ (91% based on $Mo(CO)_6$) as yellow-green crystals.

$[(C_6H_5)_4P]_2[W(NO)_2Cl_2Br_2]$.—This complex was prepared in exactly the same way as its Mo analog and was obtained in 64% yield (based on $W(CO)_6$).

$[(C_6H_5)_4P]_2[Mo(NO)_2S_4C_4(CN)_4]$.—To a solution of $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$ (1.07 g) in dichloromethane (100 ml) was added a solution of $Na_2S_2C_2(CN)_2$ (0.37 g) in methanol (50 ml). On evaporation of the resulting orange-brown solution using a water pump, a dark brown tar was formed which was extracted with dichloromethane (50 ml). This extract was filtered and treated with 2-propanol (10 ml) and the solution was evaporated using a water pump until crystallization began. After standing overnight at 0°, the solution was filtered and the dark orange-brown crystals were washed with pentane and air dried. The yield was 0.54 g (48% based on $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$).

Electronic Spectrum.—This was recorded in dichloromethane solution and yielded the following values for λ_{max} in cm^{-1} (intensities in l. mol^{-1} cm^{-1}): 12,700 (400); 19,640 (1100); 22, 520 (3600); 27,090 (6100).

$[(C_6H_5)_4P]_2[Mo(NO)_2(S_2C{=}C(CN)_2)_2]$.—This complex was prepared in the same way as its 1,2-dithiolene analog above and was obtained as orange-brown crystals in 50% yield; mp 121–123°.

Electronic Spectrum.—This was recorded in dichloromethane solution and yielded the following values for λ_{max} in cm^{-1} (intensities in l. mol^{-1} cm^{-1}): 17,700 (800); 21,900 (2700); 28,600 (2800); 30,070 (2500).

$[(C_6H_5)_4P]_2[W(NO)_2S_4C_4(CN)_4]$.—This complex was prepared in the same way as its molybdenum analog and was formed as orange-brown crystals in a yield of 45%; mp 88–89°.

Electronic Spectrum.—This was recorded in dichloromethane solution and yielded the following values for λ_{max} in cm^{-1} (intensities in l. mol^{-1} cm^{-1}): 12,500 (200); 23,900 (11,200 sh); 25,500 (13,700).

$[(C_6H_5)_4P]_2[W(NO)_2(S_2C{=}C(CN)_2)_2]$.—This complex was prepared in the same way as its molybdenum analog and was obtained in 45% yield; mp 119° dec.

Electronic Spectrum.—This was recorded in dichloromethane

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(1) Part X: J. A. McCleverty, J. Locke, B. Ratcliff, and E. J. Wharton, *Inorg. Chim. Acta*, **3**, 283 (1969).

(2) Supported by the Science Research Council of Great Britain.

(3) (S–S) refers to a bidentate sulfur ligand and not to diatomic sulfur.

(4) B. F. G. Johnson, K. H. Al-Obadi, and J. A. McCleverty, *J. Chem. Soc., A*, 1668 (1969).

(5) N. G. Connelly, J. Locke, and J. A. McCleverty, *Inorg. Chim. Acta*, **2**, 411 (1968).

(6) J. Locke and J. A. McCleverty, *Chem. Commun.*, 102 (1965).

(7) J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

(8) E. J. Wharton and J. A. McCleverty, *J. Chem. Soc., A*, 2258 (1969).

(9) R. Gomper and E. Kutler, *Angew. Chem.*, **74**, 251 (1962).

(10) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

(11) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1192 (1940).

TABLE I

ANALYTICAL AND CONDUCTIVITY DATA OBTAINED FROM NITROSYL COMPLEXES

	Analytical data, %								
	C		H		N		S		
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Λ^a
$[(C_6H_5)_4P]_2[Mo(NO)_2S_4C_4(CN)_4]$	60.3	60.0	3.6	3.4	7.5	7.2	11.5	11.1	310
$[(C_6H_5)_4P]_2[Mo(NO)_2(S_2C{=}C(CN)_2)_2]$	60.3	59.7	3.6	3.9	7.5	7.6	11.5	11.5	258
$[(C_6H_5)_4P]_2[Mo(NO)_2(S_2C_6Cl_4)_2]$	51.8	51.6	2.9	3.2	2.0	1.9	9.2	9.9[b]	240[c]
$[(C_6H_5)_4P]_2[W(NO)_2S_4C_4(CN)_4]$	55.9	55.2	3.4	3.7	7.0	6.9	10.7	10.2	277
$[(C_6H_5)_4P]_2[W(NO)_2S_2C{=}C(CN)_2)_2]$	55.9	55.4	3.4	3.7	7.0	7.5	10.7	11.4	263
$[(C_6H_5)_4P]_2[W(NO)_2(S_2C_6Cl_4)_2]$	48.7	48.4	2.7	2.9	1.9	1.8	8.7	10.0[d]	246[c]

[a] In cm² mol^{-1} ohm^{-1} in 10^{-4} *M* acetone. [b] Chlorine analysis: calcd, 20.4; found, 20.3. All other compounds have negative halogen analyses except that in *d*. [c] Measured under nitrogen. [d] Chlorine analysis: Calcd, 19.2; found, 20.9.

solution and yielded the following values for λ_{max} in cm^{-1} (intensities in l. mol^{-1} cm^{-1}): 24,900 (7600 sh); 28,100 (23,000).

$[(C_6H_5)_4P]_2[Mo(NO)_2(S_2C_6Cl_4)_2]$.—To $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$ (1.07 g) dissolved in degassed dichloromethane (100 ml) was added a degassed solution of $K_2S_2C_6Cl_4$, prepared from the reaction of tetrachlorobenzene-1,2-dithiol (0.56 g) with potassium metal (0.16 g) in ethanol (50 ml). After shaking for 3 hr, the dark brown solution was filtered and water (5 ml) was added to the filtrate. On gradual evaporation of the solution *in vacuo* a red-brown solid precipitated, which was collected by filtration and recrystallized from dichloromethane-2-propanol affording dark red-purple microcrystals. These were collected by filtration, washed with pentane, and dried under a stream of N_2. The yield of the complex was 0.4 g (29% based on $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$).

Electronic Spectrum.—This was recorded in dichloromethane solution and yielded the following values for λ_{max} in cm^{-1} (intensities in l. mol^{-1} cm^{-1}): 13,250 (500); 18,740 (1500); 28,600 (8200 sh).

$[(C_6H_5)_4P]_2[W(NO)_2(S_2C_6Cl_4)_2]$.—This complex was prepared in the same way as its molybdenum analog and was obtained as red-purple microcrystals in 17% yield; mp 123–124°.

Results and Discussion

The reactions of methanolic solutions of disodium 1,2-dicyanoethylene-1,2-dithiolate, $Na_2S_2C_2(CN)_2$, and disodium 1,1-dicyanoethylene-2,2-dithiolate, $Na_2S_2C{=}C(CN)_2$, with dichloromethane solutions containing $[(C_6H_5)_4P]_2[M(NO)_2Cl_2Br_2]$ (M = Mo or W) afforded the dark orange-brown, crystalline diamagnetic complexes $[(C_6H_5)_4P]_2[M(NO)_2S_4C_4(CN)_4]$ and $[(C_6H_5)_4P]_2[M(NO)_2(S_2C{=}C(CN)_2)_2]$, respectively. These compounds dissolve in polar solvents and in dichloromethane giving deep orange-brown solutions which are air stable. We previously reported[6] that the reaction between the polymeric $[Mo(NO)_2Cl_2]_n$ and $Na_2S_2C_2(CN)_2$ in a mixture of acetonitrile and methanol afforded *green* $Mo(NO)_2S_4C_4(CN)_4^{2-}$, but this is incorrect since, after many repetitions of this experiment under varying conditions, we failed to isolate *pure* $Mo(NO)_2S_4C_4(CN)_4^{2-}$. The dinitrosylated complex is certainly formed in this reaction, but other products appear to be $MoOS_4C_4(CN)_4^{2-}$ [1] and $MoS_6C_6(CN)_6^{2-}$,[12] both of which are *green*. It should be noted that attempts to purify the nitrosyls by chromatography (column and thin layer) led to the decomposition of the complexes. Because of these difficulties we have avoided the use of the air-sensitive polymeric nitrosyl halides $[M(NO)_2Cl_2]_n$ as precursors and have preferred to use the air-stable $M(NO)_2Cl_2Br_2^{2-}$. Reaction of these latter with dipotassium tetrachlorobenzene-1,2-dithiolate, $K_2S_2C_6Cl_4$, in ethanol afforded the red-purple $[(C_6H_5)_4P]_2[M(NO)_2(S_2C_6Cl_4)_2]$ which dissolved in degassed acetone or dichloromethane giving deep red air-sensitive solutions. The complexes, as solids, are apparently oxidized by air, reaction with the molybdenum complex being more rapid than with its tungsten analog. Treatment of $[(C_6H_5)_4P]_2[Mo(NO)_2Cl_2Br_2]$ with disodium toluene-3,4-dithiolate, $Na_2S_2C_6H_3CH_3$, in ethanol did not give the expected dianion, but a pale brown solid which was isolated from the reaction mixture may have contained the monoanion $Mo(NO)_2(S_2C_6H_3CH_3)_2^-$ although no sample sufficiently pure to give satisfactory elemental analyses could be obtained. Elemental analytical data and conductivity measurements which support our formulations of the other new compounds are given in Table I.

The complexes $M(NO)_2S_4C_4(CN)_4^{2-}$ and $M(NO)_2(S_2C_6Cl_4)_2^{2-}$ have been examined voltammetrically in dichloromethane solution using a rotating platinum electrode (Table II). The voltammograms are dominated by large irreversible anodic and cathodic waves near the extremes of the voltage scan (+1.8 to −1.8 V), but, in addition to these multielectron processes, clear one-electron[13] oxidation waves are observed in the range +0.28 to +0.52 V. No important reduction processes were observed in the voltammograms of the dithiolenes and the 1,1-dicyanoethylene-2,2-dithiolates

TABLE II

VOLTAMMETRIC DATA OBTAINED FROM MOLYBDENUM AND TUNGSTEN NITROSYL COMPLEXES

Complex	$E_{1/2}{}^a$	R^b	D^c	Process
$Mo(NO)_2S_4C_4(CN)_4^{2-}$	0.36	58	18	$-2 \rightarrow -1$
$Mo(NO)_2(S_2C_6Cl_4)_2^{2-}$	0.35	51	17	$-2 \rightarrow -1$
$W(NO)_2S_4C_4(CN)_4^{2-}$	0.52	73	15	$-2 \rightarrow -1$
$W(NO)_2(S_2C_6Cl_4)_2^{2-}$	0.28	61	2[d]	$-2 \rightarrow -1$?
$NiS_4C_4(CN)_4^{2-}$	0.05	58	18	$-2 \rightarrow -1$[e]

[a] In volts, *vs.* saturated calomel electrode containing 1 *M* LiCl, using rotating Pt electrode. [b] Reversibility criterion: $E_{3/4} - E_{1/4}$ = 56 mV for reversible one-electron process; estimated error in reading and recording potentials is ±10 mV. [c] $D = i_d/c$ in μA/mol. [d] Wave height reduced by electrode coating. [e] Chemically and electrochemically established one-electron oxidation process.

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(12) J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc., A*, 816 (1968).

(13) The number of electrons involved in these electron-transfer reactions has not been determined directly but may be inferred from the chemistry of the compounds and from comparison of i_d/c values obtained from the couple $NiS_4C_4(CN)_4^{2-} \rightleftharpoons NiS_4C_4(CN)_4^- + e^-$ obtained under conditions identical with those used for measuring the dinitrosyl (Table II).

TABLE III

NO STRETCHING FREQUENCIES OBTAINED FROM MOLYBDENUM AND TUNGSTEN DINITROSYLDITHIOLENE AND RELATED COMPLEXES

Complex	Cation	ν_{NO}, cm^{-1}		Medium
$Mo(NO)_2S_4C_4(CN)_4{}^{2-}$	$(C_6H_5)_4P^+$	1737 s	1631 s	CH_2Cl_2
	$(C_6H_5)_4P^+$	1728 s	1622 s	KBr disk
$Mo(NO)_2(S_2C{=}C(CN)_2)_2{}^{2-}$	$(C_6H_5)_4P^+$	1740 s	1630 s, br	KBr disk
$Mo(NO)_2(S_2C_6Cl_4)_2{}^{2-}$	$(C_6H_5)_4P^+$	1704 s	1595 s	KBr disk
$Mo(NO)_2(S_2C_6Cl_4)_2{}^{-}$ [a]	$(C_6H_5)_4P^+$	1773 s	1658 s	KBr disk
$Mo(NO)_2(S_2C_6H_3CH_3)_2{}^{-}$ [a]	$(C_6H_5)_4P^+$	1760 s	1650 s	KBr disk
$W(NO)_2S_4C_4(CN)_4{}^{2-}$	$(C_6H_5)_4P^+$	1705 s	1605 s	KBr disk
$W(NO)_2(S_2C{=}C(CN)_2)_2{}^{2-}$	$(C_6H_5)_4P^+$	1705 s	1611 s	KBr disk
$W(NO)_2(S_2C_6Cl_4)_2{}^{2-}$	$(C_6H_5)_4P^+$	1680 s	1585 s	KBr disk
$Mo(NO)_2(S_2CN(CH_3)_2)_2$	. . .	1770 s	1670 s	$CHCl_3$
$W(NO)_2(S_2CN(CH_3)_2)_2$	. . .	1740 s	1635 s	$CHCl_3$
$[Mo(NO)_2Cl_2]_n$ [b]	. . .	1805 s	1690 s	Nujol
$Mo(NO)_2Cl_4{}^{2-}$	$(C_6H_5)_4As^+$	1720 s	1600 s	Nujol
$Mo(NO)_2Cl_2Br_2{}^{2-}$	$(C_6H_5)_4P^+$	1770 s	1630 s	Nujol
$W(NO)_2Cl_2Br_2{}^{2-}$	$(C_6H_5)_4P^+$	1725 s	1600 s	Nujol

[a] Presumed molecular formula. [b] Contains a *cis*-dinitrosyltetrachlorometal coordination unit.

did not exhibit significant electrochemical behavior. The half-wave oxidation potentials, excepting those of $W(NO)_2(S_2C_6Cl_4)_2{}^{2-}$, occur at values within the range where normally the one-electron transfer can be effected chemically using iodine. However, only in the reaction of $Mo(NO)_2(S_2C_6Cl_4)_2{}^{2-}$ with iodine were we able to collect sufficient evidence for the formation of a monoanion. Thus, the solution of the dianion, on treatment with I_2, changed in color from red to green, and an esr signal, consisting of a six-line multiplet superimposed on a strong single line (^{95}Mo and ^{97}Mo, $I = {}^5/_2$) was detected from this solution ($\langle g \rangle = 2.0031$ and $\langle a \rangle_{Mo} = 26$ G). Similar esr data were obtained from the material believed to contain $Mo(NO)_2(S_2C_6H_3CH_3)_2{}^-$.

The dependence of $E_{1/2}$ values on the sulfur ligand substitutents is evident in all the systems investigated and follows the order observed in many other dithiolene systems, namely, that the potentials for the couple

$$M(NO)_2\text{-}(S\text{-}S)_2{}^{2-} \rightleftharpoons M(NO)_2\text{-}(S\text{-}S)_2{}^{-} + e^-$$

become increasingly negative as the electron-withdrawing properties of the sulfur ligand substituents decrease. We would expect, therefore, that the $E_{1/2}$ values for the toluene-3,4-dithiolene couple would be considerably lower than +0.35 V, and probably nearer to 0.00 V. For this reason, the dianionic species would be unstable toward oxidation under normal laboratory conditions and the complex might be preferentially isolated as a monoanion, as our experimental observations suggest.

The infrared spectra of the complexes, recorded in the region 1550–1800 cm^{-1} where stretching frequencies of NO groups terminally bound to transition metals occur,[14] contain two strong frequencies indicating that the NO groups are in a *cis* arrangement. It is not possible, using either ir or esr spectral data, to establish whether the complexes have pseudooctahedral or pseudotrigonal prismatic symmetries.

The positions of the NO stretching frequencies depend on the overall charge on the complexes and on the nature of the sulfur ligands. Thus, the average positions of the NO stretching modes in the dianionic molybdenum dithiolenes are 1720 and 1613 cm^{-1}, and, if oxidation of these species to monoanions does occur, a substantial increase in the value of ν_{NO} would be expected. Those species which we believe to contain the monoanions have these frequencies some 64 cm^{-1} higher than those in the corresponding dianions, suggesting that the monoanionic complexes are indeed formed. The dependence of ν_{NO} on the relative electron-withdrawing or -releasing properties of the sulfur ligands, which has been noted elsewhere,[15,16] is apparent in both the dianionic and (postulated) monoanionic species; *i.e.*, ν_{NO} is in the order $S_2C_2(CN)_2 > S_2C_6Cl_4 > S_2C_6H_3CH_3$. The NO stretching frequencies in $Mo(NO)_2S_4C_4(CN)_4{}^{2-}$ are higher than those in the tungsten analog, which implies that back-donation from the metal to NO is greater in the latter: this may arise as a consequence of relatively better overlap between the metal orbitals of tungsten and the π^* orbitals of NO. A comparison of ν_{NO} obtained from the dicyanodithiolene, 1,1-dicyano-2,2-dithiolate, and dithiocarbamate complexes may be made. The three types of complexes are isoelectronic, and the difference between the first two and the third is two negative charges on the basic $M(NO)_2S_4$ coordination unit. We might expect, therefore, that ν_{NO} in the dithiocarbamates would occur some 80–100 cm^{-1} higher than in the dianionic species (*cf.* the nitrosyl halides in Table III). However, the actual increase on going from the dianionic complexes to $M(NO)_2(S_2CNK_2)_2$[6] is only about 40 cm^{-1}. Previous spectroscopic studies of the dithiocarbamato ligand in metal complexes containing CO suggest[17] that the sulfur ligand is certainly not a strong π donor and its back-accepting properties are certainly curtailed by the electron-releasing $-NR_2$ group. Thus, we think the most reasonable explanation of the small increase in ν_{NO} is that the dithiolato ligands must be functioning as π acceptors which are relatively more powerful than S_2CNR_2. It may also be observed that ν_{NO} in the 1,2-dicyanodithiolenes and 1,1-dicyanoethylene-2,2-dithiolates occur at very similar values implying that the two ligand systems have similar π-acceptor properties, as observed previously.[5,15]

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(14) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(15) J. A. McCleverty, T. A. James, and E. J. Wharton, *Inorg. Chem.*, **8**, 1340 (1969).

(16) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Am. Chem. Soc.*, **89**, 6082 (1967).

(17) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).