

which water is not very highly compatible, care must be exercised in ascribing the behavior of metal ion species to the completely solvated (unhydrated) metal ion.

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The Electronic Structures of Square-Planar Metal Complexes. II.¹ The Complexes of Maleonitriledithiolate with Copper(II), Nickel(II), Palladium(II), and Platinum(II)

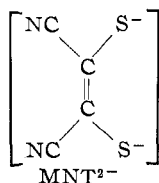
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Several square-planar metal complexes containing the dianion of maleonitriledithiol, which we call MNT, are reported. The Ni²⁺, Pd²⁺, and Pt²⁺ complexes are diamagnetic, but the presence of very low energy d-d spectral bands indicates that MNT is as weak field as Br⁻ and I⁻ in a square-planar situation. The Cu²⁺ complex is a spin doublet, as expected. The electron spin resonance (e.s.r.) spectrum of Cu(MNT)₂²⁻ is reported in several different solvents. The combined electronic spectral and e.s.r. results indicate that axial perturbations due to solvent molecules are very weak or nonexistent in these complexes.

Introduction

In a recent communication¹ we briefly described the characterization of Co²⁺ and Ni²⁺ complexes containing as ligand the dianion of maleonitriledithiol (MNT), which is shown below.



The complexes we reported first have the general formula R₂[M(MNT)₂], where R is some unipositive ion. More recently, stable complexes of the type R[M(MNT)₂] have been reported.^{2,3}

The structure of the [(C₂H₅)₄N]₂[Ni(MNT)₂] complex has been solved by a combination of three-dimensional Patterson, Fourier, and least-squares techniques.⁴ The Ni(MNT)₂²⁻ group is planar, and the Ni²⁺ is truly four-coordinate in the crystal. The [n-C₄H₉)₄N]₂[Co(MNT)₂] complex was claimed to be the first well-authenticated example of a rigorously planar, high-spin metal complex.¹ This claim has recently been challenged by Davison, *et al.*, who believe the Co(MNT)₂²⁻ complex is, in fact, low spin.⁵ In view of this situation, we shall describe our experiments on the Co(MNT)₂²⁻ complex in considerable detail in a

separate paper. The preparation, characterization, and certain physical properties of the R₂[M(MNT)₂] (with M = Cu²⁺, Ni²⁺, Pd²⁺, and Pt²⁺) complexes are described in this paper.

Experimental

Preparation of Compounds. Na₂MNT.—Sodium maleonitriledithiolate was prepared according to the published method.^{6,7} This yellow hygroscopic salt was dried and stored over calcium chloride in a vacuum desiccator until prior to use.

[(C₂H₅)₄N]₂[Ni(MNT)₂].—A solution of 3.8 g. of Na₂MNT in 17 ml. of 1:1 aqueous methanol was warmed on a steam bath. A solution of 2.4 g. of NiCl₂ in 5 ml. of aqueous methanol was added dropwise to the warm Na₂MNT solution, with stirring. The intensely red solution was filtered. To the filtrate was added a solution of 2.6 g. of (C₂H₅)₄NBr in 5 ml. of aqueous methanol. After cooling, the red precipitate which formed was filtered off. Addition to the filtrate of 1.2 g. of (C₂H₅)₄NBr in water produced more of the precipitate. The precipitates were combined, washed with water, and then dried at 60° *in vacuo*. The 6 g. of red material was recrystallized from ethanol-acetone, yielding 4.5 g. of large red crystals of [(C₂H₅)₄N]₂[Ni(MNT)₂].

The other R₂[M(MNT)₂] complexes were prepared using essentially this same procedure.

Reaction of Pd(NH₃)₄Cl₂ with Na₂MNT.—An olive-green precipitate was obtained from the reaction in aqueous solution of one equivalent of Na₂MNT and Pd(NH₃)₄Cl₂, as previously reported.⁶ This compound is a 1:1 electrolyte in DMF solution, with Λ = 95 cm.² equiv.⁻¹ ohm⁻¹. The electronic spectrum of this compound shows a band at 15,700 cm.⁻¹ (ε 80) characteristic of (R₄N)₂[Pd(MNT)₂].

Physical Measurements.—Electronic spectra were taken using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used as received. Static susceptibility measurements were made at room temperature by the Gouy method with Hg[Co(SCN)₄] as calibrant. Conductivities were deter-

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(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963); *Inorg. Chem.*, **2**, 1227 (1963).

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(6) G. Bähr and G. Schletzer, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957).

(7) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).

TABLE I
ANALYTICAL DATA FOR $R_2[M(MNT)_2]$ COMPLEXES

Complex	C		H		N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(n-C_4H_9)_4N]_2[Ni(MNT)_2]$	58.37	58.11	8.81	8.81	10.21	10.19
$[(n-C_4H_9)_4N]_2[Pd(MNT)_2]$	55.22	55.22	8.27	8.39	9.65	9.27
$[(n-C_3H_7)_4N]_2[Pd(MNT)_2]$	50.58	50.21	7.43	7.35	11.06	10.80
$[(n-C_3H_7)_4N]_2[Pt(MNT)_2]$	45.30	45.05	6.65	6.66	9.91	9.84
$[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$	47.69	47.87	6.67	6.81	13.91	13.48
$[(C_2H_5)_4N]_2[Co(MNT)_2]$	58.00	58.15	8.76	8.78	10.15	9.92
$[(C_2H_5)_4N]_2[Zn(MNT)_2]$	47.55	47.58	6.65	6.53

TABLE II
PHYSICAL PROPERTIES OF SOME $[(n-C_4H_9)_4N]_2[M(MNT)_2]$ COMPLEXES

Complex	Color	M.p., °C.	Λ^a	μ_{eff} , B.M.
$[(n-C_4H_9)_4N]_2[Ni(MNT)_2]$	Orange-red	143-145	165	Diamag.
$[(n-C_4H_9)_4N]_2[Pd(MNT)_2]$	Green	155-158	176	Diamag.
$[(n-C_4H_9)_4N]_2[Pt(MNT)_2]$	Red	164-167	167	Diamag.
$[(n-C_4H_9)_4N]_2[Zn(MNT)_2]$	Yellow	156-158	150	Diamag.
$[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$	Red-brown	125-126	150	1.85
$[(C_2H_5)_4N]_2[Cu(MNT)_2]$	Red-brown	112 dec.	186	1.78

^a Nitromethane solution.TABLE III
INFRARED SPECTRA OF SOME $[(n-C_4H_9)_4N]_2[M(MNT)_2]$ COMPLEXES

Complex	Infrared band maxima, cm^{-1}
$[(n-C_4H_9)_4N]_2[Ni(MNT)_2]$	2960, 2930, 2870, 2210, 2191, 2181, 1480, 1455, 1379, 1146, 1100, 1055, 1020, 1000, 876
$[(n-C_4H_9)_4N]_2[Pd(MNT)_2]$	2960, 2925, 2870, 2210, 2185, 1480, 1455, 1380, 1142, 1109, 1059, 1040, 1020, 880, 860
$[(n-C_4H_9)_4N]_2[Pt(MNT)_2]$	2960, 2930, 2870, 2215, 2195, 2185, 1480, 1465, 1380, 1150, 1105, 1060, 1040, 1020, 880, 860
$[(n-C_4H_9)_4N]_2[Zn(MNT)_2]$	2958, 2930, 2875, 2190, 1487, 1460, 1440, 1380, 1147, 1119, 1050, 1012, 875, 860
$[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$	2960, 2930, 2870, 2180, 1485, 1451, 1380, 1148, 1110, 1062, 1049, 1027, 1000, 874, 862
Na_2MNT	2210, 1450, 1430, 1151, 1110, 1050, 1010, 1000

mined on an Industrial Instruments bridge, Model RC16B2, using a cell calibrated with 1 M KCl solution. Infrared spectra were measured using the KBr wafer technique with a Perkin-Elmer Model 421 spectrophotometer. A Norelco X-ray machine with Cu $K\alpha$ radiation and nickel filter was used for measuring X-ray powder patterns.

The electron spin resonance (e.s.r.) measurements were made using a Varian 100 kc./sec. field modulation spectrometer that operates in the region of 9.5 kMc./sec. The concentrations of complex in the solutions employed were all approximately 0.005 M. Sample tubes were of iron-free quartz. Both the room temperature and low temperature measurements were made on the same sample.

Results

Analytical data for the $R_2[M(MNT)_2]$ complexes are given in Table I. Colors, conductances, melting points, and magnetic moments are given in Table II. The complexes all appear to be 2:1 electrolytes in

nitromethane solution.⁸ The most prominent bands in the infrared spectra are given in Table III. Examination of the infrared spectra reveals that the $C\equiv N$ stretch at about 2200 cm^{-1} in MNT is little affected by the coordination of the sulfur atoms to the metals.

Table IV gives the X-ray powder diffraction spectra of the $[(C_2H_5)_4N]_2[M(MNT)_2]$ complexes, with $M = Ni^{2+}$, Cu^{2+} , and Zn^{2+} . The Ni^{2+} and Cu^{2+} complexes are isomorphous and we conclude from this that $Cu(MNT)_2^{2-}$ is square-planar. It is of interest to note that the X-ray powder pattern for the presumably tetrahedral $[(C_2H_5)_4N]_2[Zn(MNT)_2]$ is considerably different from the others.

TABLE IV
X-RAY DIFFRACTION RESULTS FOR SOME $[(C_2H_5)_4N]_2[M(MNT)_2]$ COMPLEXES

Complex	Interplanar spacings (Å.) of the most prominent peaks
$[(C_2H_5)_4N]_2[Ni(MNT)_2]$	11.95 (vs), 8.35 (w), 6.92 (s), 6.19 (vs), 4.95 (m), 4.80 (m), 4.15 (vs), 3.98 (s), 3.47 (s), 3.20 (w), 3.12 (m), 3.06 (m)
$[(C_2H_5)_4N]_2[Cu(MNT)_2]$	12.28 (vs), 8.27 (w), 6.92 (s), 6.19 (s), 4.98 (m), 4.80 (m), 4.19 (vs), 3.95 (s), 3.47 (s), 3.14 (m), 3.04 (w)
$[(C_2H_5)_4N]_2[Zn(MNT)_2]$	7.13 (vs), 6.61 (vs), 5.47 (s), 5.21 (m), 4.27 (m), 4.21 (m), 3.95 (m), 3.46 (m), 3.08 (m), 3.00 (s), 2.96 (s)

Electron Spin Resonance.—The e.s.r. spectrum of $[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$ was measured in methanol, pyridine, and DMF at room temperature. The $\langle g \rangle$ values are nearly the same in these solvents. The spectrum in pyridine is shown in Fig. 1. The hyperfine lines due to ^{63}Cu and ^{65}Cu are resolved in the high-field ($3/2$) transition.

The e.s.r. spectrum of $Cu(MNT)_2^{2-}$ in a methanol

(8) Conductance ranges in nitromethane have been given by N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

TABLE V
 ELECTRON SPIN RESONANCE RESULTS FOR SOME CUPRIC COMPLEXES

Complex	$\langle g \rangle$ measured	$\langle A \rangle$ gauss ^b measured	g_{\parallel}	g_{\perp}	A_{\parallel} , gauss	A_{\perp} , gauss
$[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$ in Methanol, 300°K.	2.0458	75.99
Methanol glass, 77°K.	(2.044) ^a	...	2.082	2.024	158.9	43.3
DMF, 300°K.	2.0458	75.63
Pyridine, 300°K.	2.0471	75.16
$[(C_2H_5)_4N]_2[Cu(S_2C_2O_2)_2]$ in Methanol, 300°K.	2.0427	81.26
Methanol glass, 77°K.	(2.044) ^a	...	2.083	2.024	176	51
DMF, 300°K.	2.0440	81.34
$[Cu(S_2CN(C_2H_5)_2)]$ in DMF, 300°K.	2.0445	81.87

^a Calculated from g_{\perp} and g_{\parallel} . ^b ± 0.1 gauss.

glass at 77°K. is shown in Fig. 2. There are two different sets of absorption bands. The first set consists of sharp, strong bands centered at about $g = 2.0$. The other bands, marked $3/2$, $1/2$, $1/2$, and $3/2$ in Fig. 2, are definitely weaker. The weaker lines are centered about g_{\parallel} , as is also true for the resonance of glasses containing other Cu^{2+} complexes.^{9,10} The equations given by Neiman and Kivelson⁹ were used to obtain approximate¹¹ values of g_{\perp} , g_{\parallel} , A_{\perp} , and A_{\parallel} . The necessary e.s.r. measurements were made using strip chart recordings which were calibrated by the use of an n.m.r. probe and counter. Values of g_{\parallel} and A_{\parallel} given are for the nuclear quantum number assignments shown in Fig. 2. Two other Cu^{2+} complexes, $Cu(S_2C_2O_2)_2^{2-}$ and $Cu[S_2CN(C_2H_5)_2]$, were studied for comparison purposes. All the e.s.r. results are given in Table V. It may be noted that the average $\langle g \rangle$ values calculated from the values of g_{\parallel} and g_{\perp} measured in methanol glasses agree well with the $\langle g \rangle$ values obtained in the solutions.

Discussion

Weak-Field Nature of MNT.—The weak-field nature of MNT is readily demonstrated with the green $Pd(MNT)_2^{2-}$ complex. The spectrum of $Pd(MNT)_2^{2-}$ in DMF solution shows a band at $638\text{ m}\mu$ ($15,700\text{ cm}^{-1}$, $\epsilon\ 86$). This band is too intense to be spin-forbidden, and therefore is assigned to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ($x^2-y^2 \rightarrow xy$) transition in D_{2h} symmetry. This transition has orbital energy Δ_1 .¹² In Table VI are given the Δ_1 values for a number of Pd^{2+} complexes, using a value of 70 cm^{-1} for the F_4 electron-repulsion parameter for each complex. It is apparent that the sulfurs in MNT exert an even weaker field than Br^- , as judged from the values of Δ_1 given. Thus, for a square-planar situation, we are obliged to place MNT at the weak-field end of the spectrochemical series along with I^- .

(9) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 156 (1961).

(10) H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

(11) The difficulties encountered in evaluating the e.s.r. parameters are pointed out in ref. 9 and 10. The accuracy of the equations given in ref. 9 decreases as the hyperfine constants increase; see F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).

(12) See (a) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963); (b) R. F. Fenske, D. S. Martin, and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

 TABLE VI
 VALUES OF THE ORBITAL PARAMETER Δ_1 FOR
 SOME SQUARE-PLANAR METAL COMPLEXES

Complex	Δ_1 , cm^{-1a}
$Ni(MNT)_2^{2-}$	15,200 ^b
$Ni(CN)_4^{2-}$	26,000 ^c
$Pd(MNT)_2^{2-}$	18,150 ^b
$PdBr_4^{2-}$	18,450 ^b
$PdCl_4^{2-}$	19,150 ^c
$Pd(CN)_4^{2-}$	>30,000 ^c

^a $F_4 = 70\text{ cm}^{-1}$ is assumed for the Pd^{2+} complexes; $F_4 = 100\text{ cm}^{-1}$ is assumed for the Ni^{2+} complexes. ^b From spectra measured in acetone, DMF, DMSO, and pyridine. ^c From ref. 12a.

Also included in Table VI are Δ_1 values for $Ni(MNT)_2^{2-}$ and $Ni(CN)_4^{2-}$. The value of $15,200\text{ cm}^{-1}$ for $Ni(MNT)_2^{2-}$ is the smallest Δ_1 observed to date for a diamagnetic, planar metal complex. This is further evidence of the weak-field character of MNT.

Although MNT is in the weak-field category, the $d^8\text{ M}(MNT)_2^{2-}$ complexes are unusually stable. For example, we have found that the MNT group is inert to substitution by most common ligands. Even the CN^- ligand is ineffective unless present in concentrations substantially greater than the $M(MNT)_2^{2-}$ concentration. Bähr and Schleiter, who first prepared Na_2MNT , found that the reaction of $Pd(NH_3)_4^{2+}$ with one mole of MNT gives a complex with the formula $Pd(NH_3)_2(MNT)$.⁶ We find that the product of the reaction is the complex $[Pd(NH_3)_4][Pd(MNT)_2]$, which is identified by spectral and conductance measurements. This is a qualitative indication that MNT has a high *trans* effect.

Magnetic Properties of $Cu(MNT)_2^{2-}$.—The magnetic moment of $[(C_2H_5)_4N]_2[Cu(MNT)_2]$ in DMF solution is 1.96 B.M., in reasonable agreement with the value of 1.81 B.M. required for $S = 1/2$ with $\langle g \rangle = 2.0458$. The magnetic moments of the solid complexes $[(C_2H_5)_4N]_2[Cu(MNT)_2]$ and $[(n-C_4H_9)_4N]_2[Cu(MNT)_2]$ are 1.78 and 1.85 B.M., respectively, also in good agreement with the $\langle g \rangle$ value. In this connection, it is interesting to note that the magnetic moments of the solid $R[M(MNT)_2]$ complexes are all lower than expected for the observed $\langle g \rangle$ values, presumably due to exchange.⁸

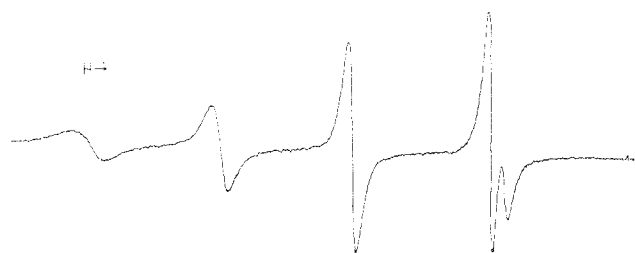


Fig. 1.—Electron spin resonance spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{-[Cu(MNT)}_2\text{]}$ in pyridine at room temperature.

The values of g_{\parallel} and g_{\perp} listed in Table V for Cu(MNT)_2^{2-} and $\text{Cu(S}_2\text{C}_2\text{O}_2)_2^{2-}$ are approximately the same, with $g_{\parallel} \approx 2.08$ and $g_{\perp} \approx 2.02$. These values may be compared with the values $g_{\parallel} = 2.254$, $g_{\perp} = 2.075$ for planar Cu(acac)_2 ,¹³ which has four oxygen donor atoms. Thus we have the expected result that the orbital contribution to the magnetic moment in both the parallel and perpendicular directions is reduced in the complexes containing sulfur as a donor atom.

Solution Structure of M(MNT)_2^{2-} Complexes.—The Pt(MNT)_2^{2-} , Pd(MNT)_2^{2-} , and, remarkably enough, the Ni(MNT)_2^{2-} and Cu(MNT)_2^{2-} complexes remain truly square-planar in strongly coordinating solvents. For example, the electronic spectra of these complexes are identical in a wide range of solvents, including acetone, DMF, and even DMSO and pyridine. The fact that the Ni(MNT)_2^{2-} complex shows no axial perturbation in pyridine sharply contrasts with the behavior of other square-planar Ni^{2+} complexes, which tend to add solvent molecules or otherwise associate to achieve a distorted octahedral arrangement of ligands.¹⁴

The fact that the e.s.r. spectrum of Cu(MNT)_2^{2-} is the same in DMF, methanol, and pyridine is further evidence of the lack of axial perturbations by solvent molecules. In the pyridine case, the resolution of the hyperfine lines due to the ^{63}Cu and ^{65}Cu nuclei is especially significant. Pyridine molecules in the fifth and sixth coordination positions would be expected to exchange rapidly and broaden the e.s.r. lines.

(13) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).

(14) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1962), and references therein.

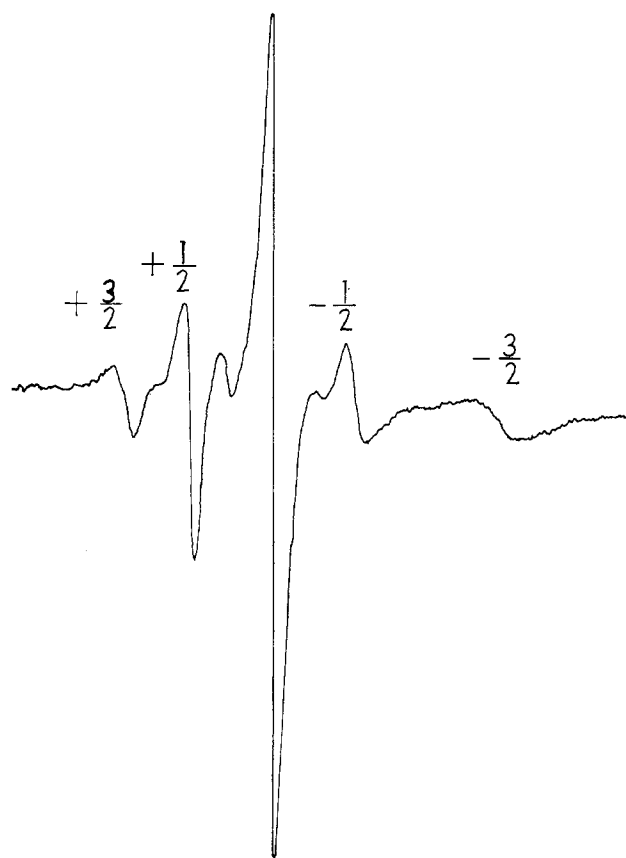


Fig. 2.—Electron spin resonance spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{-[Cu(MNT)}_2\text{]}$ at 77°K. in a methanol glass.

The unusual stability of the square-planar structure for the Ni(MNT)_2^{2-} and Cu(MNT)_2^{2-} complexes is evidence for the involvement of the $4p_z$ metal orbital in π -bonding. Axial σ -perturbations would take the metal $4p_z$ orbital out of the π -system, thus eliminating the added stability due to electronic delocalization throughout the seventeen-atom system.

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