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Transition Metal Complexes Containing 1,1-Dicyanoethylene-2,2-dithiolate

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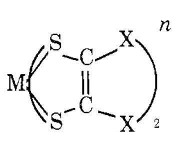
The syntheses and properties of a series of transition metal complexes containing the ligand 1,1-dicyanoethylene-2,2-dithiolate (i-mnt^{2-}) are reported. Four-coordinate complexes with the general formula $R_2[M(i\text{-mnt})_2]$ were characterized with M = Ni(II), Pd(II), Pt(II), and Cu(II), and R = $(n\text{-}C_4H_9)_4N^+$. In addition, the $R[Au(i\text{-mnt})_2]$ complex was obtained. Complexes with the general formula $R_3[M(i\text{-mnt})_3]$ were characterized with M = Co(III) and Fe(III). The Ni(II), Pd(II), and Pt(II) complexes are diamagnetic and presumably have a square-planar structure. These $M(i\text{-mnt})_2{}^{2-}$ complexes could not be readily oxidized to stable $M(i\text{-mnt})_2{}^-$ systems, in contrast to the ease of oxidation of the isomeric $M(\text{mnt})_2{}^{2-}$ complexes. The spectral and magnetic properties of the bis and tris i-mnt^{2-} complexes are discussed and compared with analogous mnt^{2-} complexes.

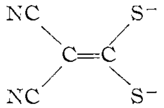
Introduction

Square-planar metal complexes containing sulfur-donor ligands of general structure I have provided many



I

unusual and interesting electronic features.[2] Of more than ordinary interest is the fact that stable complexes in system I with a given metal and ligand can occur in three different charge types, usually n = 0, −1, and −2. In order to investigate the role of the ligand structure in stabilizing the n = 0 and −1 complexes, we have examined the behavior of complexes containing 1,1-dicyanoethylene-2,2-dithiolate (i-mnt^{2-}), shown below (II).



i-mnt^{2-}
II

The ligand i-mnt^{2-} is a geometrical isomer of maleonitriledithiolate (mnt^{2-}), one of the most thoroughly studied ligands in the system I complexes.

The preparation, characterization, and certain physical properties of the $R_2[M(i\text{-mnt})_2]$ (with M = Ni(II), Pd(II), Pt(II), and Cu(II)), $R_3[M(i\text{-mnt})_3]$ (with M=Co(III), Fe(III)), and $R[Au(i\text{-mnt})_2]$ complexes are described in this paper.

Experimental Section

Preparation of Compounds. **$Na_2(i\text{-mnt})$.**—Sodium 1,1-dicyanoethylene-2,2-dithiolate was prepared according to a published method.[3] The pale yellow salt was used without further purification.

$[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$.—A solution of 1.8 g. of $NiCl_2 \cdot 6H_2O$ in 10 ml. of methanol was added dropwise, with stirring, to a solution of 2.4 g. of $Na_2(i\text{-mnt})$ in 15 ml. of methanol. The green-gold solution was filtered. The filtrate was added to a stirred solution of 4.47 g. of $(n\text{-}C_4H_9)_4Br$ in 10 ml. of methanol. After cooling, the green-gold precipitate which formed was filtered off. The precipitate was washed with ether and then air dried. The essentially quantitative yield of green-gold material was recrystallized from hot methanol yielding needles of $[(n\text{-}C_4H_9)_4N]_2$-$[Ni(i\text{-mnt})_2]$ melting at 191–192°.

The most prominent bands in the infrared spectrum of $[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$ are at 2950, 2925, 2862, 2180, 1600, 1478, 1445, 1390, 1370, 1220, 1170, 1090, 1040, 1012, 987, 960, 925, 880, and 735 cm.$^{-1}$. The infrared spectra of the other i-mnt^{2-} complexes reported in this paper are essentially the same. The most prominent bands in the infrared spectrum of $Na_2(i\text{-mnt})$ are at 3500, 3300, 2180, 1630, 1370, 1220, 950, and 880 cm.$^{-1}$. It is interesting that the $-C{\equiv}N$ stretching frequency at 2180 cm.$^{-1}$ is not affected by the coordination of the sulfur atoms of the ligand to the central metal.

$[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$.—A solution of 0.17 g. of $CuCl_2 \cdot 2H_2O$ in 5 ml. of methanol was added dropwise, with stirring, to a solution of 0.39 g. of $Na_2(i\text{-mnt})$ in 10 ml. of methanol. The dark red solution was filtered and the filtrate added dropwise to a stirred solution of 0.65 g. of $(n\text{-}C_4H_9)_4NBr$ in 10 ml. of methanol. The tan precipitate was filtered off and washed with ethanol–water, then finally with ether. After the precipitate had been air dried, the tan material was recrystallized from hot methanol, yielding red-brown needles $[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$ melting at 172–175°. In addition, during recrystallization an orange material decomposing at 280° was isolated, but not further identified.

The other $[(n\text{-}C_4H_9)_4N]_2[M(i\text{-mnt})_2]$ complexes, as well as $[(n\text{-}C_4H_9)_4N][Au(i\text{-mnt})_2]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(i\text{-mnt})_3]$, were prepared using essentially the same procedure as described for $[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$.

$[(n\text{-}C_4H_9)_4N]_3[Co(i\text{-mnt})_3]$.—A solution of 1.15 g. of $Na_3Co(CO_3)_3 \cdot 3H_2O$, which was prepared by the published procedure,[4] and 1.73 g. of $Na_2(i\text{-mnt})$ was mixed and dissolved in methanol. The solution was heated on a steam bath for 15 min. The filtrate was cooled and added dropwise to a stirred solution of 2.98 g. of $(n\text{-}C_4H_9)_4NBr$ in methanol–water. On standing green-gold crystals formed from this solution. The crystals were filtered, washed with ether, and air dried. Recrystallization from 2-propanol gave needles melting at 173–174°.

Physical Measurements.—Electronic spectra were taken on 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 determined on an Industrial Instrument Model RC 16 B2 bridge, using a cell calibrated with 0.010 M KCl solution. Infrared spectra were measured with a Perkin-Elmer Model 421 spectrophotometer using the KBr wafer technique. Polarographic measurements

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[1] Alfred P. Sloan Research Fellow, 1964–1966.

[2] References are collected in H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 240 (1965).

[3] R. Gomper and E. Kutler, *Angew. Chem.*, **74**, 251 (1962).

[4] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

TABLE I

ANALYTICAL DATA FOR THE METAL–i-mnt COMPLEXES[a]

Complex	C, %		H, %		N, %		S, %		Metal, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$	58.30	58.29	8.81	8.78	10.20	10.92				
$[(n\text{-}C_4H_9)_4N]_2[Pd(i\text{-mnt})_2]$	55.11	54.97	8.33	8.39	9.64	10.13				
$[(n\text{-}C_4H_9)_4N]_2[Pt(i\text{-mnt})_2]$	50.02	50.03	7.56	7.49	8.75	8.88	13.35	13.52	20.31	20.40[b]
$[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$	57.95	57.39	8.77	8.47	10.14	10.34	15.47	15.60		
$[(n\text{-}C_4H_9)_4N][Au(i\text{-mnt})_2]$	40.06	39.87	5.21	5.01	9.74	9.84				
$[(n\text{-}C_4H_9)_4N]_3[Co(i\text{-mnt})_3]$	59.71	59.39	9.04	9.17	10.45	10.57	15.94	15.85		
$[(n\text{-}C_4H_9)_4N]_3[Fe(i\text{-mnt})_3]$	59.85	59.75	8.97	8.99	10.47	10.83				

[a] All analytical results are from Galbraith Laboratories, Knoxville, Tenn. [b] As ash.

were made in DMF solution with a dropping mercury electrode in a three-electrode cell, using an electronic polarograph described elsewhere.[5] Oscillopolarography was employed, a platinum electrode serving as indicator electrode. Silver–silver perchlorate was used as the reference electrode: $[Ag|AgClO_4(0.1\ M)]$; $[(n\text{-}C_3H_7)_4N][ClO_4]$ (0.1 M). Solutions were approximately 0.001 M in complex and 0.1 M in tetra-n-propylammonium perchlorate. Electron spin resonance (e.s.r.) spectra were measured with a Varian 100 kc./sec. field modulation spectrometer operating in the region of 9.5 kMc./sec. A Norelco X-ray machine with copper Kα radiation and nickel filter was used for measuring X-ray powder patterns.

TABLE II

PHYSICAL PROPERTIES OF METAL–i-mnt COMPLEXES

Complex	Color	M.p., °C.[a]	Λ[b]	μ_{eff}, B.M.
$[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$	Green-gold	191.5–192.5	151	Diamag.
$[(n\text{-}C_4H_9)_4N]_2[Pd(i\text{-mnt})_2]$	Orange	207	162	Diamag.
$[(n\text{-}C_4H_9)_4N]_2[Pt(i\text{-mnt})_2]$	Yellow	223–224	174	Diamag.
$[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$	Red-brown	172–175	174	1.79
$[(n\text{-}C_4H_9)_4N][Au(i\text{-mnt})_2]$	Orange	185–186	61	...
$[(n\text{-}C_4H_9)_4N]_3[Co(i\text{-mnt})_3]$	Green-gold	173–174	210	Diamag.
$[(n\text{-}C_4H_9)_4N]_3[Fe(i\text{-mnt})_3]$	Green	130	205	5.89[c]

[a] All melting points are uncorrected. [b] In cm.^{2} mole^{-1} ohm^{-1} in 10^{-3} M nitromethane solutions. [c] Average of several measurements.

TABLE III

X-RAY DIFFRACTION RESULTS [INTERPLANAR SPACINGS (Å.) CORRESPONDING TO MOST PROMINENT PEAKS] FOR SOME $[(n\text{-}C_4H_9)_4N]_2[M(i\text{-mnt})_2]$ COMPLEXES

$[(n\text{-}C_4H_9)_4N]_2[Ni(i\text{-mnt})_2]$

13.39 (vs), 10.79 (w), 9.81 (s), 9.51 (m), 7.9 (m), 7.20 (vs), 6.92 (m), 6.65 (s), 6.51 (m), 5.83 (w), 5.43 (vs), 5.31 (vs), 4.82 (m), 4.72 (m), 4.25 (vs), 4.11 (vs), 3.95 (vs), 3.66 (vs), 3.34 (m)

$[(n\text{-}C_4H_9)_4N]_2[Pd(i\text{-mnt})_2]$

13.39 (w), 10.79 (s), 9.71 (m), 9.31 (vw), 8.51 (m), 7.25 (m), 6.46 (m), 5.83 (m), 5.43 (m), 5.31 (m), 4.90 (m), 4.15 (s), 4.00 (s), 3.75 (s), 3.63 (m)

$[(n\text{-}C_4H_9)_4N]_2[Pt(i\text{-mnt})_2]$

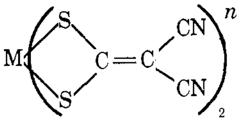
13.39 (s), 10.79 (w), 9.71 (s), 9.11 (w), 8.76 (w), 7.97 (m), 7.25 (s), 5.43 (m), 5.31 (s), 4.93 (s), 4.85 (m), 4.44 (s), 4.17 (s), 3.98 (s), 3.79 (s), 3.74 (s), 3.63 (m)

$[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$

13.19 (m), 10.79 (s), 9.71 (s), 8.27 (m), 7.20 (s), 6.46 (w), 5.83 (m), 5.44 (s), 5.34 (s), 4.85 (m), 4.58 (m), 4.19 (m), 4.08 (vs), 4.00 (vs), 3.91 (vs), 3.72 (s), 3.66 (s), 3.64 (m), 3.33 (m)

Results

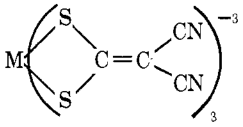
Analytical data for the $R_x[M(i\text{-mnt})_y]$ complexes are given in Table I. Analytical values for the complexes with M = Ni(II), Pd(II), Pt(II), Cu(II), and Au(III) are in agreement with the formulation III.



III

$n = -2$ for Ni(II), Pd(II), Pt(II), and Cu(II)
$n = -1$ for Au(III)

The complexes isolated with M = Fe(III) and Co(III) have the formula indicated by IV.



IV

M = Co(III), Fe(III)

Colors, conductances, and decomposition or melting points are given in Table II. In nitromethane solution, the Ni(II), Pd(II), Pt(II), and Cu(II) complexes are 2:1 electrolytes and the Co(III) and Fe(III) complexes are 3:1 electrolytes, whereas the conductance of the Au(III) complex is in the range of a 1:1 electrolyte.[6] Table III gives the X-ray powder diffraction spectra of the $[(n\text{-}C_4H_9)_4N]_2[M(i\text{-mnt})_2]$ complexes with M = Ni(II), Pd(II), Pt(II), and Cu(II). These compounds are all isomorphous and from the magnetic data we conclude that they are all square-planar.

The e.s.r. spectrum of $[(n\text{-}C_4H_9)_4N]_2[Cu(i\text{-mnt})_2]$ was measured at room temperature in acetone solution. The hyperfine lines due to ^{63}Cu and ^{65}Cu were resolved in the high-field transition. The values $\langle g \rangle = 2.046$ and $\langle A \rangle = 75.9$ gauss were obtained.

Reversible polarographic waves could only be obtained for the Ni and Pd complexes in the reaction $M(i\text{-mnt})_2^{2-} + e^- \rightleftarrows M(i\text{-mnt})_2^{3-}$. The half-wave potentials for M = Ni and M = Pd are −2.2 and −2.33 v., respectively, as measured in DMF solution relative to a Ag–AgClO$_4$ reference electrode. No reversible oxidation waves were observed for any of the complexes.

The visible and ultraviolet absorption spectra of the complexes in acetonitrile solution are set out in Table IV. Measurements in other solutions show that the spectra are not solvent dependent.

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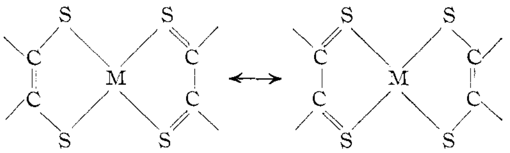
[5] M. C. Kelley, J. D. Fisher, and K. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); **32**, 1262 (1960).

[6] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

Discussion

Probably of greatest interest is the fact that, unlike the $\mathrm{M(mnt)_2^{2-}}$ complexes, the $\mathrm{M}(i\text{-mnt})_2^{2-}$ complexes cannot be easily oxidized to stable $n = -1$ complexes by electrolytic or chemical means. Thus, we infer that the unusual $n = 0$ and -1 complexes of system I are stabilized by π-electron delocalization in the $\mathrm{MS_2C_2}$ five-membered rings. For example, in the $n = 0$ complexes the two equivalent valence-bond structures V and VI offer a reasonable mechanism of π electron delocalization.[7]


V VI

It is significant that analogous structures cannot be written for the proposed neutral $\mathrm{M}(i\text{-mnt})_2$ complexes.

A detailed analysis of the electronic spectra presented in Table IV is postponed pending a complete molecular orbital calculation. At the present time, however, it is possible to catalog the bands according to transition type The intensities of the lowest energy bands in the $\mathrm{Ni}(i\text{-mnt})_2^{2-}$, $\mathrm{Pd}(i\text{-mnt})_2^{2-}$, and $\mathrm{Co}(i\text{-mnt})_3^{3-}$ complexes indicate that the electronic transitions are spin-allowed and between molecular orbitals derived from d valence orbitals. It has been observed that the lowest d–d band occurs at about the same energy in planar Ni(II) and six-coordinate Co(III) complexes containing the same ligand.[8] The positions of the lowest bands in $\mathrm{Ni}(i\text{-mnt})_2^{2-}$ and $\mathrm{Co}(i\text{-mnt})_3^{3-}$ fall within the narrow range 15,000–15,700 cm.$^{-1}$ and thus are consistent with the d–d assignments. We further suggest that the lowest energy intense band in each of the square-planar complexes be assigned as a $\mathrm{M \rightarrow L^*}$ intramolecular charge transfer, in view of the energy relationship $\mathrm{Ni}(i\text{-mnt})_2^{2-} < \mathrm{Pd}(i\text{-mnt})_2^{2-} > \mathrm{Pt}(i\text{-mnt})_2^{2-} < \mathrm{Au}(i\text{-mnt})_2^{-}$ characteristic of this type of transition.[9]

Assuming that the first band in $\mathrm{Ni}(i\text{-mnt})_2^{2-}$ and $\mathrm{Pd}(i\text{-mnt})_2^{2-}$ arises from the transition $^1\mathrm{A_g} \rightarrow {}^1\mathrm{B_{1g}}$ $(x^2 - y^2 \rightarrow xy)$ in $\mathrm{D_{2h}}$ symmetry, we may calculate values for the orbital parameter Δ_1 and compare them with the Δ_1 values of other $\mathrm{MS_2X}$ planar four-membered ring systems and certain related $\mathrm{MS_2C_2}$ planar five-membered ring complexes. These comparisons are listed in Table V. It is a striking fact that the Δ_1 values in the four-membered ring cases are in a narrow range between 17,300 and 18,600 cm.$^{-1}$. Substituent effects on Δ_1 are larger in the five-membered ring system, where the span is 14,500–20,500 cm.$^{-1}$. Of special interest is the fact that Δ_1 for $\mathrm{Ni}(i\text{-mnt})_2^{2-}$ is 4000 cm.$^{-1}$ larger than Δ_1 for the isomeric $\mathrm{Ni(mnt)_2^{2-}}$ complex. This comparison shows the effect of ligand structure on the splitting of molecular orbital levels.

Table IV

Electronic Spectra of Metal–i-mnt Complexes and $\mathrm{Na_2}(i\text{-mnt})$[a]

$\tilde{\nu}_{\max}$, cm.$^{-1}$ (ϵ)	Assignment
$\mathrm{Ni}(i\text{-mnt})_2^{-2}$	
15,700 (87)	d → d
22,100 (3×10^4)	M → L*
29,600 (6×10^4)	L → L*
34,400 sh (2×10^4)	...
37,900 (2.3×10^4)	L → L*
$\mathrm{Pd}(i\text{-mnt})_2^{-2}$	
22,300 sh (300)	d → d
26,500 (6.6×10^4)	M → L*
31,800 (3.8×10^4)	L → L*
39,600 (1.5×10^4)	L → L*
48,800 sh (8×10^3)	...
$\mathrm{Pt}(i\text{-mnt})_2^{-2}$	
24,200 (5.5×10^4)	M → L*
28,400 (3.5×10^3)	L → L*
32,100 sh (1.8×10^4)	L → L*
35,900 (3.6×10^4)	...
40,000 sh (1.4×10^4)	L → L*
44,500 sh (1.6×10^4)	...
47,600 (3.3×10^4)	...
$\mathrm{Au}(i\text{-mnt})_2^{-}$	
21,700 (320)	d → d
25,000 sh (660)	d → d
28,600 (11.7×10^4)	M → L*
29,800 sh (8.3×10^4)	L → L*
31,200 (5.3×10^4)	L → L*
36,400 ($7{,}4 \times 10^3$)	...
41,500 (1.2×10^4)	...
$\mathrm{Cu}(i\text{-mnt})_2^{-2}$	
15,100 sh (550)	d → d
22,200 (1.5×10^4)	...
28,600 (8.0×10^4)	...
29,600 sh (4.3×10^4)	L → L*
32,000 sh (2.5×10^4)	L → L*
37,400 sh (1.1×10^4)	L → L*
$\mathrm{Co}(i\text{-mnt})_3^{-3}$	
15,000 (517)	d → d
24,900 (3.6×10^4)	...
29,600 (6.2×10^4)	L → L*
33,800 sh (3.2×10^4)	...
40,000 sh (2.1×10^4)	L → L*
$\mathrm{Fe}(i\text{-mnt})_3^{-3}$	
15,600 (8.9×10^3)	...
19,000 (5.8×10^3)	...
[22,500 (1.1×10^4)]	b
26,300 sh (2.7×10^4)	...
29,400 (7×10^4)	L → L*
[33,100 (4×10^4)]	c
36,400 (2.2×10^4)	...
42,300 sh (6×10^3)	...
$\mathrm{Na_2}(i\text{-mnt})$	
29,100 (1.9×10^3)	...
31,400 sh (1.2×10^3)	...
38,600 sh (300)	...
39,600 sh (340)	...
49,500 (2.2×10^3)	...

[a] All spectra in acetonitrile. Spectra measured in pyridine, acetone, and DMF are essentially the same as in acetonitrile. [b] Only observed in pyridine. [c] Only observed in DMF.

The orbital splittings in the tris complexes are in the critical range which produces a low-spin $\mathrm{Co}(i\text{-mnt})_3^{3-}$

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(7) G. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon-Addison-Wesley, Reading, Mass., 1962, p. 123.

(9) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

TABLE V

THE VALUE OF Δ_1 IN SOME PLANAR MS_4 COMPLEXES
$F_2 = 10F_4 = 800$ cm.$^{-1}$ for Ni(II)
$F_2 = 10F_4 = 600$ cm.$^{-1}$ for Pd(II) and Pt(II)

Complex	Ring	Δ_1, cm.$^{-1}$	Complex	Ring	Δ_1, cm.$^{-1}$
$Ni(mnt)_2^{2-}$	MS_2C_2	14,500[a]	$Ni(dto)_2^{2-}$	MS_2C_2	20,500[e]
$Ni(tdt)_2^{2-}$	MS_2C_2	17,300[b]	$Pd(mnt)_2^{2-}$	MS_2C_2	17,800[a]
$Ni(dtp)_2$	MS_2P	17,300[c]	$Pd(dtp)_2$	MS_2P	23,900[c]
$Ni(exan)_2$	MS_2C	18,300[c]	$Pd(i\text{-}mnt)_2^{2-}$	MS_2C	24,400
$Ni(i\text{-}mnt)_2^{2-}$	MS_2C	18,500	$Pd(dto)_2^{2-}$	MS_2C_2	28,100[e]
$Ni(dtc)_2$	MS_2C	18,600[c]			
$Ni(dmpt)_2^{2-}$	MS_2C_2	19,000[d]			

[a] Spectrum from S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964). [b] Spectrum from R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966). tdt^{2-} = toluene-3,4-dithiolate. [c] Spectrum from C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962). $dtp^- = {}^-S_2P(OC_2H_5)_2$; $exan^- = {}^-S_2COC_2H_5$; $dtc^- = {}^-S_2CN(C_2H_5)_2$. [d] Spectrum quoted in D. L. Leussing, *J. Am. Chem. Soc.*, **81**, 4208 (1959). dmp^{2-} = 2,3-dimercaptopropanol. [e] Spectrum from A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965); dto^{2-} = dithiooxalate.

TABLE VI

COMPARISON OF SOLUTION E.S.R. RESULTS AND THE POSITIONS OF THE LOWEST ELECTRONIC BAND IN $Cu^{II}S_4$ PLANAR COMPLEXES[a]

Complex	Solution	$\langle g \rangle$	$\langle A \rangle$, gauss	Lowest band, cm.$^{-1}$ (ϵ)
$Cu(mnt)_2^{2-}$	DMF	2.046	75.6 (^{63}Cu,^{65}Cu)[b]	8,300 (100)[d]
$Cu(tdt)_2^{2-}$	DMF	2.046	77.6 (^{63}Cu,^{65}Cu)[c]	10,450 (40)[e]
$Cu(dtc)_2$	DMF	2.045	81.9 (^{63}Cu,^{65}Cu)[b]	16,300 (107)
$Cu(dto)_2^{2-}$	DMF	2.044	81.3 (^{63}Cu,^{65}Cu)[b]	17,200 (275)[f]
$Cu(i\text{-}mnt)_2^{2-}$	Acetone	2.046	75.9 (^{63}Cu,^{65}Cu)	15,100 (550)[g]

[a] All measurements were made at room temperature. [b] From E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964). [c] From R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966). [d] From J. H. Waters and H. B. Gray, *ibid.*, **87**, 3534 (1965). [e] R. Williams, unpublished results; spectrum in THF solution. [f] Spectrum in aqueous solution. [g] Spectrum in DMF solution.

complex and a high-spin $Fe(i\text{-}mnt)_3^{3-}$ complex. The room temperature magnetic moment of 5.89 B.M., indicating $S = {}^5/_2$ for $Fe(i\text{-}mnt)_3^{3-}$, may be compared with 4.24 B.M. for $Fe(dtc)_3$, in which $S = {}^5/_2$ and $S = {}^1/_2$ spin states are believed to exist in thermal equilibrium.[10] It is of interest to compare these two complexes, since the Δ_1 planar splittings in $Ni(i\text{-}mnt)_2^{2-}$ and $Ni(dtc)_2$ are within 100 cm.$^{-1}$.

The e.s.r. spectrum of $Cu(i\text{-}mnt)_2^{2-}$ in acetone solution is essentially identical with that of $Cu(mnt)_2^{2-}$.[11] In analogy to $Cu(mnt)_2^{2-}$ we assign a ground state $^2B_{1g}[\ldots(xy)^1]$ to the $S = {}^1/_2$ $Cu(i\text{-}mnt)_2^{2-}$ complex. A comparison of g and A values in several $Cu^{II}S_4$ planar systems is given in Table VI. The g values are all in the small range 2.044–2.046 and the A ($^{63,65}Cu$) values are between 75 and 82 gauss. Furthermore, in all cases measured the $g_{\parallel}$ and $g_{\perp}$ values are essentially independent of the exact structure of the $Cu^{II}S_4$ complex.[2] This is true even though the Δ_1 values obtained from the first electronic spectral band are quite dissimilar, spanning the range 8330–17,200 cm.$^{-1}$. In order to understand this striking fact we suggest that the highest-filled molecular orbital of $x^2 - y^2$ symmetry, which is most probably involved in the lowest band, is mainly composed of sulfur orbitals. Thus the first excited state in this scheme would not contribute strongly in determining the value of $g_{\parallel}$. The excited states which affect the $g_{\parallel}$ and $g_{\perp}$ values (the unpaired electron has mainly metal d character) are thought to be of higher energy and not significantly separated.[12]

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(11) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

(12) NOTE ADDED IN PROOF.—Professor John P. Fackler, Jr., Case Institute of Technology, has kindly informed us that he and D. Concouvanis have independently prepared certain of the $i\text{-}mnt^{2-}$ complexes described in this paper: *Chem. Commun.* (London), to be published.