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Reactions of Dithiolene Complexes with Amines. I. Adducts of Iron and Cobalt Complexes

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The formation of adducts of $[M(mnt)_2]_2^{2-}$ and $[M(tfd)_2]_2^{2-}$, M = Fe, Co (mnt ≡ maleonitriledithiolate, tfd ≡ 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate), with primary, secondary, tertiary, and heterocyclic monodentate and bidentate amines in solution and the crystalline state is described. With monodentate amines (L) the equilibria are $[M(mnt)_2]_2^{2-} + 2L \rightleftharpoons 2[M(mnt)_2L]^-$ (K_1) and $[M(mnt)_2L]^- + L \rightleftharpoons [M(mnt)_2L_2]^-$ (K_2), with $K_1(\mathrm{Fe}) > K_1(\mathrm{Co})$ and $K_2(\mathrm{Fe})/K_1(\mathrm{Fe}) \ll K_2(\mathrm{Co})/K_1(\mathrm{Co})$. The five-coordinate mono adducts $[M(mnt)_2L]^-$ are high spin; $S = {}^3/_2$ (Fe) and $S = 1$ (Co; possibly $S = 0$ ground state, with $S = 1$ at $+20\ \mathrm{cm}^{-1}$). At room temperature only cobalt forms six-coordinate bis-amine adducts, $[Co(mnt)_2L_2]^-$, which are diamagnetic and exist as two stereoisomers, one of which is cis octahedral. The one isolable pyridine adduct is $[Co(mnt)_2(py)_2]^-$, not $[Co(mnt)_2py]^-$.

Introduction

We are investigating three types of reactions of amines with transition metal dithiolene complexes,[1] namely, coordinative adduct formation reactions, dithiolene ligand substitution reactions, and electron-transfer reactions producing reduced dithiolene complexes and oxidized amines.[2] Coordinative equilibria may be mechanistically precursory in substitution and electron-transfer reactions, and therefore it is necessary that the characteristics and principles of adduct formation be well understood. This paper reports studies of adduct formation between iron and cobalt dithiolene complexes and a variety of aliphatic, aromatic, and heterocyclic amines, including a description of the formation equilibria in solution and of the spectral, magnetic, and stereochemical properties of the amine adducts formed. Previous studies[3-7] of similar systems are extended and several misinterpretations in the literature are corrected.

A further reason for investigation of the extent of amine adduct formation arises out of the utilization of hindered amines and their conjugate acids as noncoordinating, nonnucleophilic buffer components in nonaqueous solution, in reactions involving dithiolene complexes, oxygen, thiols, and other acid-base reactants.

Experimental Section

Reagents. Na_2mnt was prepared by the method of Krespan.[8] Amines were purified as follows and stored over molecular sieves: *n*-butylamine, 2-aminopropane, cyclohexylamine, piperidine, and ethylenediamine were distilled from potassium hydroxide pellets; benzylamine, *N,N*-dimethylbenzylamine, tri-*n*-propylamine, *N,N*-dimethylaniline, *N,N*-diethylaniline, pyridine, and 2,6-dimethylpyridine were distilled from calcium hydride; morpholine was distilled from sodium; aniline was vacuum distilled from powdered zinc and used immediately; 3-azabicyclo[3.2.2]nonane (abn) was vacuum sublimed; 1,4-diazabicyclo[2.2.2]octane (dabco) was recrystallized from heptane in the presence of sodium hydroxide pellets; 2-aminopyridine, 4-cyanopyridine and 2-methylimidazole were recrystallized from acetone–heptane; imidazole and *o*-phenylenediamine were recrystallized from benzene; hydrazine was used as the monohydrate; phenylhydrazine was distilled and stored under nitrogen. Solvent acetonitrile was distilled once from calcium hydride and then from P_4O_{10} and stored over 3A molecular sieves. Nitrobenzene was distilled prior to use.

Physical Measurements. Electronic spectra were obtained with Cary 14 and Beckman DK-2A spectrophotometers, using cells of path length 0.01–2.5 cm. The temperature of the sample solution was not rigorously controlled; however care was taken, particularly in the near-ir region, to avoid temperature variations of more than a few degrees from ambient (22°). Nmr spectra were obtained on a Varian A-60 spectrometer, in CD_3CN at normal probe temperature, with TMS as internal reference. Solid-state magnetic susceptibility data were obtained with a Faraday balance.[9]

Tetra-*n*-butylphosphonium salts of the dithiolene complexes were employed because they are more soluble than tetraalkylammonium salts in inert solvents.

$(n\text{-}Bu_4P)_2[Co(mnt)_2]_2$. The convenient large-scale procedure used here is slightly different from the literature syntheses[5,10] of $(n\text{-}Bu_4N)_2[Co(mnt)_2]_2$. Na_2mnt (20 g, 0.107 mol) was dissolved in 400 ml of 95% ethanol, under nitrogen, at 50°. To this solution was added a solution of $CoCl_2 \cdot 6H_2O$ (13 g, 0.055 mol) in 95% ethanol (100 ml). While stirring at 50° a slurry of iodine (14 g, 0.055 mol) in ethanol was added, and the stirring was continued until all iodine had dissolved. $n\text{-}Bu_4PCl$ (17 g, 0.058 mol), dissolved in a mixture of 50 ml of ethanol and 50 ml of water, was slowly added with stirring, during which time the product separated as large black crystals, which were filtered, washed with 2-propanol, and recrystallized twice from acetone–2-propanol at room temperature; mp 187°.

$(n\text{-}Bu_4P)_2[Fe(mnt)_2]_2$. To a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (4.1 g, 0.01 mol) in ethanol–water (100 ml, 1:1 by volume) was added a solution of Na_2mnt (3.7 g, 0.02 mol) in 1:1 ethanol–water (100 ml). A solution of $n\text{-}Bu_4PCl$ (3.3 g, 0.011 mol) in ethanol (100 ml) was then added. A black oil formed. Pyridine (75 ml) and water (100 ml) were added to the mixture. The resulting red-brown crystalline precipitate was collected by filtration, redissolved in chloroform (200 ml), and filtered. The chloroform solution was stirred vigorously with a solution of 20 ml of concentrated sulfuric acid in 200 ml of water, whereupon the chloroform solution became gray-green and a black precipitate formed. The precipitate was collected by filtration, washed with water, and recrystallized once from dichloromethane–chloroform–heptane and once from dichloromethane–heptane.

$(n\text{-}Bu_4P)[Co(mnt)_2(py)_2]$. Two grams of $(n\text{-}Bu_4P)_2[Co(mnt)_2]_2$ was dissolved in 15 ml of pyridine, the solution was filtered, and benzene (40 ml) was added. The green microcrystalline precipitate was collected by filtration, washed with benzene and diethyl ether, and air-dried.

An identical sample was obtained by dissolving 2.0 g of $(n\text{-}Bu_4P)_2[Co(mnt)_2]_2$ and 2.0 ml of pyridine in dichloromethane, adding 2-propanol, and evaporating the dichloromethane at room temperature until crystallization was complete. The crystals were washed with 2-propanol and air-dried.

On heating at *ca.* 180° *in vacuo* this compound lost all pyridine and reverted to the parent dimer. Weight loss data are reported in Table I.

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[1] Review: J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968). The abbreviation (S-S,R) represents the bidentate dithiolene ligand $S_2C_2R_2$. Other abbreviations used are mnt when R ≡ CN and tfd when R ≡ CF_3.

[2] I. G. Dance, T. R. Miller, and J. E. Cline, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, INOR 7.

[3] C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 2956 (1964).

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[8] E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968).

[9] Mr. J. Kleppinger is thanked for these measurements.

[10] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

Table I. Analytical Data[a]

	% C	% H	% N	% S	Wt loss[a,b]
$(Bu_4P)_2[Co(mnt)_2]_2$	47.78 (48.14)	6.10 (6.06)	9.22 (9.36)	21.29 (21.42)	
$(Bu_4P)[Co(mnt)_2(py)_2]$[c]	53.85 (53.95) [51.38]	6.20 (6.13) [6.10]	10.62 (11.10) [10.33]	17.24 (16.94) [18.92]	20.45 (20.90) [11.7]
$(Bu_4N)[Co(mnt)_2(py)_2]$[c]					20.79 (21.38) [11.97]
$(Bu_4P)[Co(mnt)_2(piperidine)]$[d]	50.78 (50.93) [53.10]	6.83 (6.93) [7.60]		18.72 (18.75) [16.68]	12.49 (12.45) [22.14]
$(Bu_4P)[Co(mnt)_2(morpholine)]$	49.15 (49.03)	6.85 (6.61)		19.73 (18.70)	12.83 (12.70)
$(Bu_4P)[Co(mnt)_2(abn)]$[e]	52.76 (53.09)	7.03 (7.10)		18.77 (17.72)	*f*
$(Bu_4P)[Co(mnt)_2(PhCH_2NH_2)_2]$[c]	55.85 (56.14) [52.75]	6.83 (6.69) [6.43]		16.14 (15.78) [18.17]	25.70 (26.36) [15.18]
$(Bu_4P)[Co(mnt)_2(BuNH_2)_2]$[c]	51.17 (51.59) [50.05]	7.82 (7.85) [7.05]		16.57 (17.22) [19.10]	19.80 (19.63) [10.89]
$(Bu_4N)[Co(mnt)_2(BuNH_2)_2]$					20.17 (20.09)
$(Bu_4P)[Co(mnt)_2(imidazole)_2]$[c]			15.78, 14.26 (15.25) [12.60]		18.32 (18.53) [10.21]
$(Bu_4P)[Co(mnt)_2(1\text{-methylimidazole})_2]$[c]			15.06 (14.69) [12.34]		21.80 (21.52) [12.05]
$(Bu_4N)[Co(mnt)_2(4,4'\text{-dipy})]$	55.01 (55.34)	5.91 (6.01)	13.05 (13.29)	17.42 (17.38)	
$(Bu_4P)_2[Fe(mnt)_2]_2$	48.66 (48.39)	5.92 (6.09)	9.32 (9.41)	20.83 (21.53)	
$(Bu_4N)[Fe(mnt)_2(NH_3)]$	49.83 (48.38)	6.70 (6.60)	14.43 (14.10)		
$(Bu_4N)[Fe(mnt)_2(n\text{-}BuNH_2)]$[d]	51.26 (51.59)	7.27 (7.27)		18.81 (19.68)	12.8 (11.2) [20.2]
$(Bu_4N)[Fe(mnt)_2(t\text{-}BuNH_2)]$	51.80 (51.59)	6.76 (7.27)		19.65 (19.68)	
$(Bu_4N)[Fe(mnt)_2(PhCH_2NH_2)]$	54.34 (54.29)	6.61 (6.61)		18.78 (18.70)	15.0 (15.6)
$(Bu_4N)[Fe(mnt)_2(piperidine)]$	52.28 (52.46)	7.44 (7.14)		19.27 (19.32)	13.7 (12.8)
$(Bu_4N)[Fe(mnt)_2(morpholine)]$	50.06 (50.51)	6.78 (6.87)		19.17 (19.26)	
$(Bu_4N)[Fe(mnt)_2(abn)]$[e]	54.38 (54.60)	7.26 (7.30)		17.60 (18.22)	
$(Bu_4N)[Fe(mnt)_2(4\text{-cyanopyridine})]$	52.95 (52.77)	5.80 (5.89)		18.35 (18.78)	
$(Bu_4N)[Fe(mnt)_2(2\text{-aminopyridine})]$	51.54 (51.77)	6.27 (6.29)		18.19 (19.06)	
$(Bu_4N)[Fe(mnt)_2(imidazole)]$			15.40 (15.16)	19.22 (19.83)	
$(Bu_4N)[Fe(mnt)_2(1\text{-methylimidazole})]$			15.05 (14.84)	18.80 (19.41)	
$(Bu_4N)[Fe(mnt)_2py]$					12.6 (12.0)
$(Bu_4N)[Fe(mnt)_2(dabco)_{1/2}]$	50.85 (51.09)	6.71 (6.67)	13.43 (13.23)		
$(Bu_4N)[Fe(tfd)_2(en)_{1/2}]$	37.39 (37.64)	4.84 (5.05)	1.81 (1.76)	15.63 (16.08)	

[a] All results reported as follows: found percentage (percentage calculated for formulation given) [calculated for alternative formulation footnoted]. [b] Percentage weight loss after removal of amine by heating at *ca.* 180°, *in vacuo*, to constant weight. [c] Brackets contain calculated values for the mono-amine adduct. [d] Brackets contain calculated values for the bis-amine adduct. [e] abn ≡ 3-azabicyclo[3.2.2]nonane, dabco = 1,4-diazabicyclo[2.2.2]octane. [f] Complex reduced to $[Co(mnt)_2]^{2-}$ on heating.

$(n\text{-Bu}_4\text{N})[\text{Co(mnt)}_2(\text{py})_2]$. $(n\text{-Bu}_4\text{N})_2[\text{Co(mnt)}_2]_2$ (1.0 g) was dissolved in the minimum volume (*ca.* 20 ml) of pyridine, the solution was filtered, and 2-propanol (10 ml) was added. The green crystals that formed on cooling were collected by filtration, washed with 2-propanol and ether, and air-dried.

$(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2(\text{imidazole})_2]$. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (0.5 g) and imidazole (0.6 g) were dissolved in 30 ml of dichloromethane and 35 ml of isobutyl alcohol. On slow evaporation of the dichloromethane, an oil formed and eventually crystallized. The crystals were collected by filtration, washed with diethyl ether, and air-dried.

$(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2(1\text{-methylimidazole})_2]$. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (1.0 g) was dissolved in acetone (50 ml) and 1-methylimidazole (1 ml) was added. After filtration 2-propanol (50 ml) was added, the acetone was slowly evaporated at room temperature, and the green crystals which formed were collected by filtration, washed with 2-propanol and diethyl ether, and air-dried.

$(n\text{-Bu}_4\text{N})[\text{Co(mnt)}_2(4,4'\text{-dipy})]$. $(n\text{-Bu}_4\text{N})_2[\text{Co(mnt)}_2]_2$ (0.58 g) was dissolved in acetone (25 ml) and 4,4′-dipyridyl (0.17 g) was added. The green solution was filtered, and crystallization began in the filtrate. 2-Propanol (20 ml) and water (5 ml) were added and the acetone was slowly evaporated at room temperature. The olive green crystals were collected by filtration, washed with 2-propanol and diethyl ether, and air-dried; mp 196–197°.

$(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2(\text{NH}_3)_2]$. Tan, beautifully crystalline samples of a complex surmised to have this composition were obtained by several methods.

A. A solution of $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (1.0 g) in dichloromethane (50 ml) was treated with dry ammonia gas, resulting in a rapid color change from dark coffee brown to light golden brown. Addition of 2-propanol (30 ml) and solvent removal on the rotary evaporator produced golden brown crystals, which were collected by filtration and washed with 2-propanol. On drying (in air or partial vacuum) the crystals reverted during 1 hr to the black crystals of the parent dimer. A good analysis of the tan crystals was not obtained.

B. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (0.1 g) was dissolved in acetonitrile (10 ml) and concentrated aqueous ammonia solution (3 ml) was added. The tan platelets which rapidly formed in the yellow-brown solution were filtered and washed with water without change, but after evaporation of the superfluous water, they rapidly reverted to the parent dimer.

C. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$, dissolved in the minimum volume of pyridine and treated with concentrated aqueous ammonia solution produced the same tan crystalline product, which could not be separated without change.

D. $(\text{Et}_4\text{N})_2[\text{Co(mnt)}_2]_2$ or $(\text{pyMe})_2[\text{Co(mnt)}_2]_2$ (pyMe^+ = *N*-methylpyridinium cation), when suspended in concentrated aqueous ammonia solution, changed crystal form during 10 min to tan microcrystalline precipitates, which decomposed on separation and drying.

Primary Amine Adducts, $(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2\text{L}_2]$, L = *n*-Butylamine, Benzylamine, Cyclohexylamine, 2-Aminopropane. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (1.0 g) was dissolved in dichloromethane, and the amine (*ca.* 2 ml) was added, followed by 2-propanol. The solution was yellow-brown. During slow evaporation of the dichloromethane at room temperature brown crystals of the adduct were formed. They were separated by filtration, washed with 2-propanol, and air-dried.

$(\text{Et}_4\text{N})[\text{Co(mnt)}_2(\text{PhNHNH}_2)_2]$. $(\text{Et}_4\text{N})_2[\text{Co(mnt)}_2]_2$ (1.0 g) was slurried in dried monoglyme (30 ml), and phenylhydrazine was added dropwise until all of the solid dissolved with formation of an orange-brown solution. Anhydrous diethyl ether was added slowly with stirring as the tan-brown crystals developed. After filtering and washing with anhydrous ether the crystals changed form while air-drying, leading to a mixture which contained some $[\text{Co(mnt)}_2]^{2-}$.

Adduct with Hydrazine. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (0.2 g) was slurried in acetonitrile (10 ml) and several drops of hydrazine was added. The yellow-brown bis adduct color was produced immediately. After addition of isobutyl alcohol and filtration, the acetonitrile was evaporated from the filtrate on the rotary evaporator, with occasional further dropwise addition of hydrazine hydrate, until incipient precipitation of an oil. To this stage the behavior of the hydrazine adduct preparation was identical with that with primary amines. On cooling to 0° red-brown crystals were obtained. They were filtered, washed with isobutyl alcohol and ether, and air-dried. The product was readily shown to be contaminated with the reduced complex $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]$ by extraction with dichloromethane.

Secondary Amine Adducts, $(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2\text{L}]$, L = Piperidine, Morpholine, 3-Azabicyclo[3.2.2]nonane. $(n\text{-Bu}_4\text{P})_2[\text{Co(mnt)}_2]_2$ (1 g) was dissolved in dichloromethane (50 ml) and 3 ml of the amine was added to produce a green solution. 2-Propanol was added and the dichloromethane was evaporated at room temperature. The green crystals which were formed were filtered, washed with 2-propanol, and air-dried.

In the presence of water at concentrations above *ca.* 0.1 *M* and at temperatures above ambient, basic secondary amines such as these undergo other reactions with $[\text{Co(mnt)}_2]_n^{n-}$, leading to orange or bright red solutions (the latter being due to the formation of $[\text{Co(mnt)}_2]^{2-}$); consequently these conditions should be avoided in the synthesis of adducts.

Adduct with 1,4-Diazabicyclo[2.2.2]octane (dabco). To $(n\text{-Bu}_4\text{N})_2[\text{Co(mnt)}_2]_2$ (1.0 g) slurried in dichloromethane (35 ml) was added dabco (1.0 g), and the resulting green-brown solution was filtered. The crystals which form on addition of heptane (20 ml) were collected by filtration, washed with ether, and air-dried. The product, mp 195–200°, was contaminated with $[\text{Co(mnt)}_2]^{2-}$ salts.

Adducts $(n\text{-Bu}_4\text{N})[\text{Fe(mnt)}_2(\text{amine})]$. These were prepared by addition of excess amine to a solution or slurry of $(n\text{-Bu}_4\text{N})_2[\text{Fe(mnt)}_2]_2$ in acetone or dichloromethane, followed by filtration of the resulting red solution. An alcohol, either 2-propanol or isobutyl alcohol, was added, and the solvent was evaporated with a rotary evaporator. The black crystals which formed were collected by filtration, washed with alcohol and ether, and air-dried.

Analysis by weight loss on distillation of the amine from the adduct is in general more definitive than elemental microanalysis in establishing adduct composition. Samples were heated at 180°, *in vacuo*, to constant weight. The results are listed in Table I.

Results

The most generally characteristic and diagnostic property of the species to be described is the electronic spectrum in the region 5–50 kK. Frequently these spectra involve many maxima and shoulders with a wide range of intensities, and significant differences between species often appear as somewhat subtle variations of spectral intensity and profile, which are not adequately documented by tabulations of frequencies and intensities. Accordingly, accurate figures displaying all pertinent spectra are incorporated in the microfilm version of this paper, and representative spectra only are portrayed here. The microfilm figures are distinguished with an M in text references below.[11]

Solvation and Dimerization Equilibria in the Absence of Amines. The parent complexes $[\text{Fe(mnt)}_2]_2^{2-}$, $[\text{Co(mnt)}_2]_2^{2-}$, $[\text{Fe(tfd)}_2]_2^{2-}$, and $[\text{Co(tfd)}_2]_2^{2-}$ are dimeric in the solid state.[12,13] In the common solvents acetonitrile, dichloromethane, acetone, nitrobenzene, and alcohols these complexes may be involved in dissociation and solvation equilibria which are clearly apparent in the concentration and solvent dependence of the spectra (Figures M1–M4). Interpretations and derived equilibrium constants are presented in Table II. For both dithiolene ligands the iron complexes are more susceptible to dissociation and solvation than their cobalt analogs.[14,15] Intense absorptions at 7.5 and 15.7 kK are characteristic of dimeric $[\text{Co(mnt)}_2]_2^{2-}$ and $[\text{Fe(mnt)}_2]_2^{2-}$, respectively.

Amine Adducts of Iron Complexes in Solution. Spectra of dichloromethane solutions of $[\text{Fe(mnt)}_2]_2^{2-}$, 2×10^{-3} *M* total iron, were recorded in the presence of varying concentrations of the monodentate amines imidazole, pyridine, 4-cyanopyridine, 2-aminopyridine, 2,6-dimethylpyridine, diethylamine, tri-*n*-propylamine,[16] and aniline. Figure 1, for imidazole, is representative of the spectral changes and isosbestic

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(11) See paragraph at end of paper regarding supplementary material.

(12) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

(13) R. Eisenberg, *Progr. Inorg. Chem.*, 12, 295 (1970).

(14) The results presented here for relatively weakly solvating conditions are consistent with those reported earlier[15] for more strongly coordinating solvents DMSO and DMF.

(15) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 43 (1966).

(16) With sterically hindered and strongly basic amines such as tri-*n*-propylamine there is slow decomposition apparently due to alkaline hydrolysis.

Table II. Dimerization and Solvation Equilibria[a]

Compd	Solvent	Result
$[Co(mnt)_2]_2^{2-}$ [b]	CH_3CN	Dimeric, concentration independent down to 10^{-4} M[a]
	CH_2Cl_2	Dimeric, concentration independent
	$PhNO_2$	Dimeric, concentration independent to 2×10^{-5} M
$[Co(tfd)_2]_2^{2-}$ [c]	CH_3CN	$K_{ass}{}^{d} = (2.7 \pm 0.5) \times 10^3\ M^{-1}$
	CH_2Cl_2	$K_{ass} = (6.5 \pm 0.5) \times 10^2\ M^{-1}$
	Acetone	$K_{ass} = (1.3 \pm 0.2) \times 10\ M^{-1}$
$[Fe(mnt)_2]_2^{2-}$ [b]	CH_3CN	Dissociated
	CH_2Cl_2	Dimeric, concentration independent down to 2×10^{-4} M
	Acetone	Dissociated
	$PhNO_2$	Dimeric
	CH_2Cl_2 + solvent	$[Fe(mnt)_2]_2^{2-} + 2(\text{solvent}) \xrightleftharpoons{K_1} 2[(\text{solvent})Fe(mnt)_2]^-$ Solvent = CH_3CN, $K_1{}^{e} = (1.4 \pm 0.5) \times 10^{-3}\ M^{-1}$ Solvent = CH_3OH, $K_1 = (3 \pm 2) \times 10^{-2}\ M^{-1}$ Solvent = t-BuOH, $K_1 = (1.0 \pm 0.5) \times 10^{-3}\ M^{-1}$
	$CH_3CN + CH_3OH$	Competitive solvation $K = [Fe(mnt)_2(CH_3CN)^-][CH_3OH]/[Fe(mnt)_2(CH_3OH)^-][CH_3CN] = 4 \times 10^{-2}$
$[Fe(tfd)_2]_2^{2-}$ [c]	CH_3CN	$K_{ass} = (6 \pm 1) \times 10^2\ M^{-1}$
	CH_2Cl_2	Dimeric, $K_{ass} > 10^5\ M^{-1}$
	Acetone	$K_{ass} = (3 \pm 2) \times 10^2\ M^{-1}$

[a] All expressions of concentration, except representation of the dimeric species in equilibrium quotients, are per single metal unit. [b] As n-Bu_4P^+ salt. [c] As n-Bu_4N^+ salt. [d] K_{ass} = [dimer]/[monomer]^2. [e] $K_1 = [(\text{solvent})Fe(mnt)_2^-]^2/[[Fe(mnt)_2]_2^{2-}][\text{solvent}]^2$.

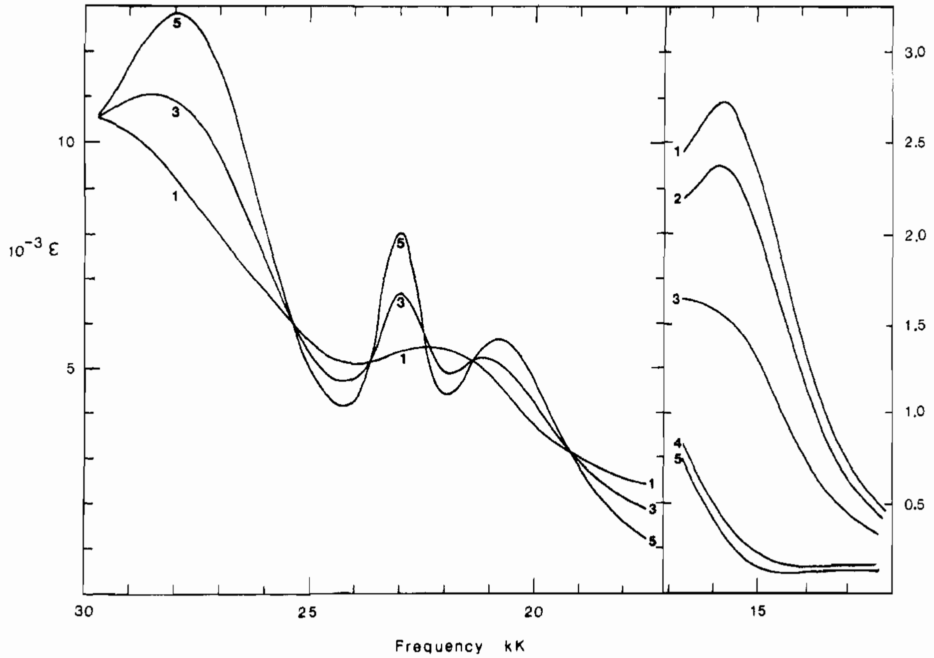

Figure 1. Spectra of dichloromethane solutions of $(Bu_4P)[Fe(mnt)_2]$, 2.0×10^{-3} M, containing imidazole at the following concentrations: 1, 0; 2, 3.0×10^{-4} M; 3, 1.0×10^{-3} M; 4, 2.0×10^{-3} M; 5, 3.0×10^{-3} M.

points observed. The spectral changes are complete at an imidazole to iron molecular ratio of 1.5, and there are no further changes at higher imidazole concentrations, indicating that the observed adduct spectrum is that of a mono adduct, $[(\text{imidazole})Fe(mnt)_2]^-$. No evidence was found for the formation of bis adducts in solution with any amine at ambient temperature. Formation constants for the mono adducts are listed in Table III; they correlate primarily with the amine steric bulk but also with the amine Bronsted basicity.

The spectra of the adducts depend on the electronic structure of the amine, as shown in Figure 2 for extreme cases with 4-cyanopyridine and imidazole. The spectra of the aniline adduct and of $[Fe(mnt)_2(CH_3CN)]^-$ are similar to the 4-cyanopyridine adduct spectrum, while the spectra of alkylamine adducts and of $[Fe(mnt)_2(CH_3OH)]^-$ are similar to that of the imidazole adduct, and the pyridine and 2-aminopyridine adduct spectra are intermediate.

Bidentate ligands (N-N) dimethylglyoxime, biacetyl dihydrazone, and biacetyl bisanil, but not o-phenylenediamine, produce spectral changes (particularly an intense absorption in the 10-11-kK region) characteristic of the spin-doublet adducts $[(N\text{-}N)Fe(mnt)_2]^-$ previously described for 1,10-phenanthroline, 2,2'-dipyridyl, and ethylenediamine.[4,17] Analogous experiments with $[Fe(tfd)_2]^-$ in acetonitrile revealed the 10-11-kK band with 1,10-phenanthroline, 2,2'-dipyridyl, and biacetyl dihydrazone, but very large excesses of dimethylglyoxime or biacetyl bisanil were required to effect the same spectral changes, indicating the low formation constants for these latter α-diimine ligands. Acetonitrile

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(17) J. K. Yandell and N. Sutin, *Inorg. Chem.*, 11, 448 (1972).

Table III. Amine Adduct Formation Constants

$$K_1 = \frac{[[(\text{amine})\text{M}(\text{mnt})_2]^-]^2}{[[\text{M}(\text{mnt})_2]^{2-}][\text{amine}]^2} \qquad K_2 = \frac{[[(\text{amine})_2\text{M}(\text{mnt})_2]^-]}{[[(\text{amine})\text{M}(\text{mnt})_2]^-][\text{amine}]}$$

Amine (pK_a, aq)	K_1 (M ≡ Fe)[a] (in CH_2Cl_2), M^{-1}	K_1 (M ≡ Co)[b] (in CH_3CN), M^{-1}	K_2 (M ≡ Co)[b] (in CH_3CN), M^{-1}
Imidazole (6.95)	$>5 \times 10^5$	$>10^4$	10^3
2-Methylimidazole (7.85)		10^3	10
Pyridine[c] (5.25)	$>5 \times 10^5$	10^2–10^3 (10^3 [d])	10
2-Aminopyridine (6.82)	$(3 \pm 1) \times 10^4$		
4-Cyanopyridine (1.90)	$(7 \pm 2) \times 10^3$	10^{-1}	
2,6-Dimethylpyridine (6.6)	$(2 \pm 1) \times 10$	*e*	
Aniline (4.63)	$(2 \pm 0.5) \times 10$	3×10^{-3} [d]	
Benzylamine (9.33)		$>10^4$	10^2
Diethylamine (10.49)	$(4 \pm 1) \times 10^5$	5[d]	
Morpholine (8.33)		10^3	10
dabco[f] (8.60)		10^3	10^{-1}
Tri-*n*-propylamine (10.65)	7 ± 3	*e*	

[a] Calculated from absorbance changes at 15.7 kK. [b] Based on absorbance changes at 7.5 and 14.3 kK. [c] K_1(Co) = 3.5 × 10^3, K_2(Co) = 5.5, in acetone: C. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 2956 (1964). [d] Value in nitrobenzene. [e] No detectable adduct formation. [f] 1,4-diazabicyclo[2.2.2]octane.

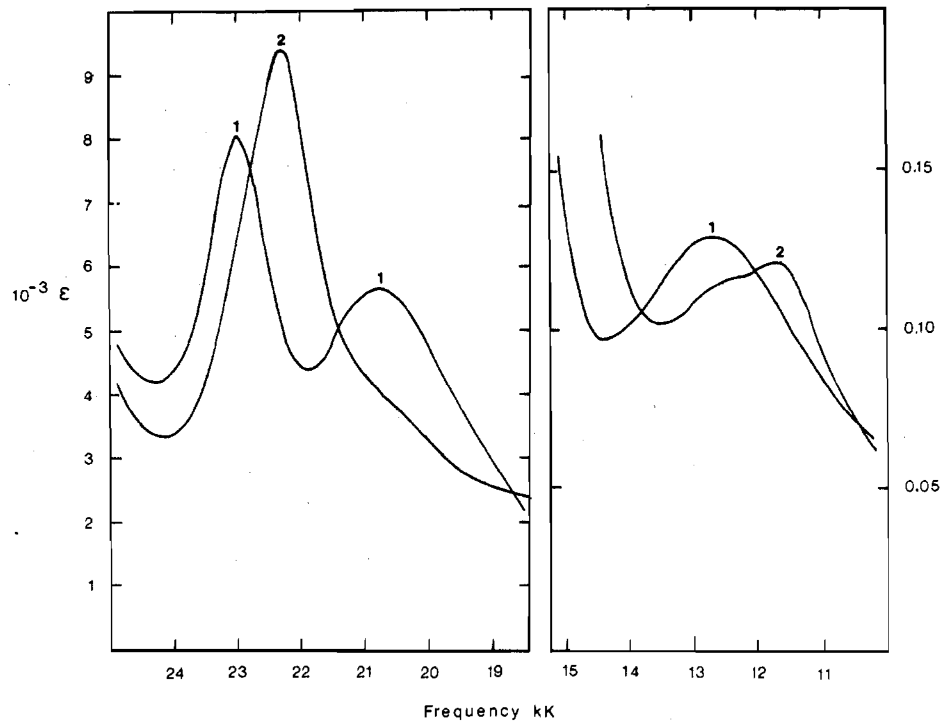

Figure 2. Spectra of dichloromethane solutions of $(Bu_4P)[Fe(mnt)_2]$, 2.10 × 10^{-3} *M*, containing (1) imidazole, 3 × 10^{-3} *M*, and (2) 4-cyanopyridine, 1.0 × 10^{-1} *M*.

solutions of ethylenediamine and $[Fe(tfd)_2]^-$ at room temperature yielded a spectrum identical with that produced by monodentate alkylamines, with the 10-11-kK band absent. Further color changes were observed when these solutions were cooled to *ca.* −45°. These observations are interpreted in terms of coordination of only one ethylenediamine nitrogen to each $Fe(tfd)_2^-$; the isolation of a compound with composition $(Bu_4P)_2[(tfd)_2Fe(H_2NCH_2CH_2NH_2)Fe(tfd)_2]$ from such solutions at room temperature corroborates this interpretation.

Isolation and Characterization of Iron Complex Amine Adducts. Crystalline samples of adducts $(Bu_4N)[Fe(mnt)_2L]$, L = ammonia, *n*-butylamine, *tert*-butylamine, benzylamine, piperidine, morpholine, 3-azabicyclo[3.2.2]nonane (abn), 2-aminopyridine, and 4-cyanopyridine, were isolated from dichloromethane or acetone solutions in the presence of excess amine. With diamines 1,4-diazabicyclo[2.2.2]octane (dabco) and ethylenediamine the complexes $(Bu_4N)_2[(mnt)_2Fe(dabco)Fe(mnt)_2]$ and $(Bu_4P)_2[(tfd)_2Fe(en)Fe(tfd)_2]$ crystallized from solution. Analytical data are contained in Table I. The solids are stable in air and showed little tendency to revert to the parent dimer on standing. Only impure adduct samples were obtained with trimethylamine and 2-methylimidazole, while attempted isolation of adducts with diethylamine, triethylamine, tri-*n*-propylamine, aniline, and *p*-phenylenediamine yielded oils which would not crystallize. The formation of adducts with basic amines is complicated by the susceptibility of iron dithiolene complexes to basic hydrolysis. Although no hydrolysis occurs in a solution containing water and pyridine, the addition of water to acetone or acetonitrile solutions containing $[Fe(mnt)_2]^-$ and an alkylamine initiates substitution processes leading to the formation and subsequent hydrolysis of $[Fe(mnt)_3]^{3-,2-}$.

Diffuse reflectance spectra of the crystalline adducts are almost identical with the respective solution spectra, except for some small frequency shifts. Room-temperature magnetic susceptibility data (see Table IV) are consistent with spin-quartet ground states for the five-coordinate iron complexes and provide no evidence for magnetic interaction between iron atoms in $[(mnt)_2Fe(dabco)Fe(mnt)_2]^{2-}$.

Characterization of Adducts of $[Co(mnt)_2]^-$ in Solution. The formation of amine adducts was followed by recording complete spectra of acetonitrile solutions of $[Co(mnt)_2]_2{}^{2-}$, total cobalt 10^{-3} *M*, in the presence of widely varied concentrations of amines. Spectral traces for illustrative concentrations of pyridine are shown in Figure 3, and analogous presentations for imidazole, 2-methylimidazole, morpholine, dabco, and benzylamine are recorded in Figures M5-M9. Figure 4 contains plots of the extinction coefficient at key frequencies *vs.* the logarithm of the total pyridine concentration over the range 5×10^{-4} to 12.4 *M* (neat). The important conclusions to be drawn from the data in Figures 3 and 4 follow. (i) Isosbestic points are maintained at 13.6, 15.3, 24.4, and 28.3 kK for solutions containing up to *ca.* 4×10^{-3} *M* pyridine. (ii) Moderately good isosbestic points occur at 22.2, 23.5, and 29.3 kK for solutions containing 1×10^{-2} through 1×10^{-1} *M* pyridine. (iii) The decrease in intensity at 7.5 kK parallels that at 12.5 kK and is complete by 3×10^{-2} *M* pyridine. Both of these absorptions are characteristic of the dimer $[Co(mnt)_2]_2{}^{2-}$, and their disappearance reflects its conversion into pyridine adducts. (iv) The formation of the first pyridine adduct is reflected in the intensity changes at 14.3, 22.7, and 27.0 kK (Figure 4), and the concentration of this adduct is maximized at *ca.* 10^{-2} *M* pyridine. The characteristic absorption maxima for this species are at 14.3 and 26.7 kK; there are also maxima at 22.4 and 39.3 kK, but these are not fully characteristic as they appear also in the spectrum of the parent dimer. This adduct species is formulated as the mono adduct, $[Co(mnt)_2py]^-$. (v) Intensity changes at 14.3, 22.7, 24.4, 27.0, 28.2, and 32.6 kK manifest the formation of a second pyridine adduct at total pyridine concentrations greater than 10^{-2} *M* with formation essentially complete at *ca.* 2 *M* pyridine.[18] The spectrum of this adduct is comprised of a weak maximum at 14.5 kK and characteristic maxima at 22.75 and 32.5 kK. This species is formulated as the bis adduct $[Co(mnt)_2(py)_2]^-$.

The pattern of spectral changes with increasing amine concentration is essentially the same for all amines investigated, with one important exception. Whereas all mono adduct spectra are very similar, there are two distinct classes of bis adduct spectra. This differentiation is clearly apparent in the three representative spectra in Figure 5. All bis adducts with primary alkylamines (including ammonia, hydrazine, and phenylhydrazine) are brown in acetonitrile, with absorption peaks at *ca.* 23, 34, and 37 kK, the peak at 34 kK being most intense, but the bis adducts of heterocyclic amines of the pyridine, imidazole, and piperidine classes are light green, with an additional absorption at about 15 kK, maxima at 23, 32, and 38 kK, and greatest intensity at 38 kK. The 15-kK peak of the green bis adducts is not residual 14.5-kK mono adduct absorption.

Table IV. Magnetic Susceptibility Data

Compd	T, °K	$10^6\chi_M$, cgsu	μ, BM
$(n\text{-}Bu_4N)[Fe(mnt)_2(piperidine)]$	296	5967	3.87[a]
$(n\text{-}Bu_4N)[Fe(mnt)_2(dabco)_{1/2}]$	296	6018	3.89[a]
$(n\text{-}Bu_4P)[Fe(tfd)_2(en)_{1/2}]$	296	5528	3.75[a]
$(n\text{-}Bu_4P)[Co(mnt)_2(PhCH_2NH_2)_2]$	296	−540 to −610	0
$(n\text{-}Bu_4P)[Co(mnt)_2(py)_2]$	296.3	−350 to −400	0
$(n\text{-}Bu_4P)[Co(mnt)_2(morpholine)]$	297.4	3070	2.87[a]
$(n\text{-}Bu_4P)[Co(mnt)_2(piperidine)]$	296.5	3105	2.89[a]
	272	3529	2.82[b]
	239	3871	2.76[b]
	205	4513	2.76[b]
	190	4896	2.76[b]
	174	5037	2.75[b]
	159	5847	2.76[b]
	144	6476	2.76[b]
	129	7180	2.75[b]
	113	8104	2.73[b]
	104	8822	2.73[b]
	94	9570	2.70[b]

[a] Calculated using the following diamagnetic corrections (cgsu): $n\text{-}Bu_4P$, −228; $n\text{-}Bu_4N$, −207; $[Fe(tfd)_2]$, $[M(mnt)_2]$, −112; amines, -60×10^{-6}. [b] Calculated using the least-squares calculated total susceptibility correction for model B (see text).

The second (green) type of bis adduct spectrum is indistinguishable from the class of spectra (Figure M10) obtained from $[Co(mnt)_2(N\text{-}N)]^-$, N-N = ethylenediamine, 1,10-phenanthroline, 2,2′-dipyridyl, and $[Co(mnt)_3]^{3-}$. This spectral similarity strongly suggests that the green bis-amine adducts exist with cis-octahedral stereochemistry analogous to that known for $[Co(mnt)_2(1,10\text{-}phen)]^-$.[13,19] The stereochemistry of the other class of bis-amine adducts cannot be adduced from the spectra alone.

While two different classes of bis adduct spectra are observed in acetonitrile, dichloromethane, or acetone, in certain other media the primary alkylamines as well as pyridine and imidazole give the "green" type of bis adduct spectrum. Figure 6 presents the spectrum of $Co(mnt)_2{}^-$ in neat *n*-butylamine and in mixtures of *n*-butylamine with benzene and with acetonitrile. It is postulated that these spectral changes which occur as the medium is varied are due to a solvation-dependent equilibrium between the two stereoisomers. The poor isosbestic point at 17.6 kK is probably due to the known negative solvatochromism of the cis-octahedral adduct.[20]

Spectra of the different amine adduct species for various amines are given in Table V. There are absorption peaks clearly diagnostic of each species: 7.5 and 12.5 kK for the dimer; 14.3-14.5 and 27 kK for the five-coordinate mono adduct; 32-33 kK for six-coordinate bis adducts.

Due to the overlapping equilibria, precise determinations of amine adduct formation constants were not attempted. Order of magnitude estimates are contained in Table III. The degree of adduct formation by 1-methylimidazole is very similar to that of imidazole, as benzimidazole is similar to 2-methylimidazole. Addition of ammonia (gas or aqueous solution) to $[Co(mnt)_2(py)_2]^-$ in pyridine solution produces color changes and crystallization indicative of complete formation of $[Co(mnt)_2(NH_3)_2]^-$. For the following amines green solutions characteristic of adduct formation are observed, but the adduct equilibria have not been further investigated: pyrazine, trimethylamine, *tert*-butylamine, 3,5-dimethylpyridine, hexamethylenetetramine. Amines for

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(18) When the solution composition is changed from 3 *M* pyridine to neat pyridine there is an abrupt change in absorption intensity over most of the spectrum, although not between 14 and 16 kK. This change, which is observed similarly for other liquid amines, is presumed to reflect a change in solvent structure in the adduct solvation sphere.

(19) G. P. Khare and R. Eisenberg, *Inorg. Chem.*, **9**, 2211 (1970).

(20) Negative solvatochromism, a shift of an absorption band to higher energy in more polar media, is readily detected for complexes $[Co(mnt)_2(N\text{-}N)]^-$. Frequencies of the lowest energy maximum of $(Bu_4P)[Co(mnt)_2(en)]$ are 16.50 kK in acetonitrile, 16.26 kK in dichloromethane, and 16.21 kK in 1:4 dichloromethane-toluene (v/v).

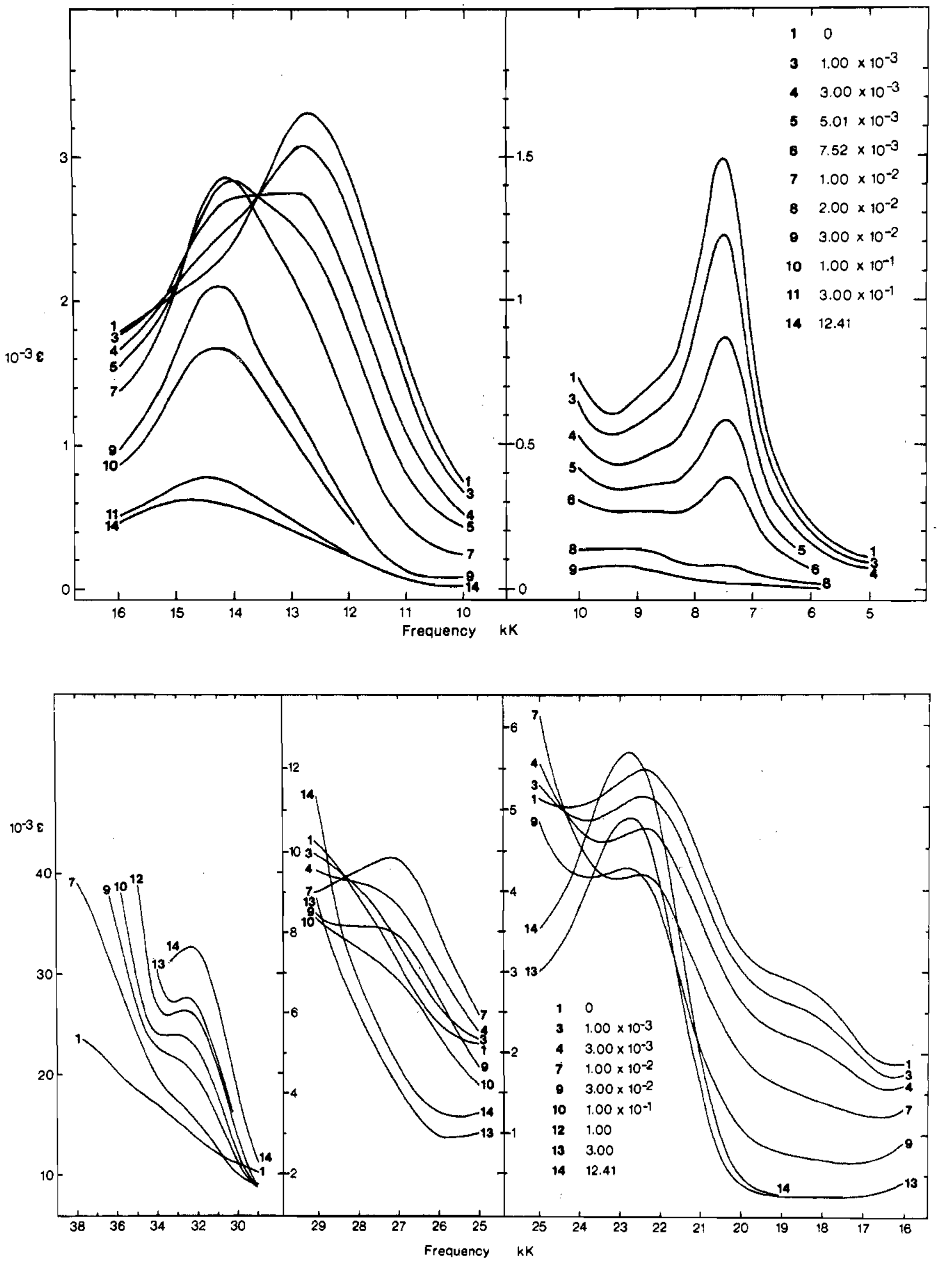


Figure 3. Spectra of acetonitrile solutions of $(n\text{-Bu}_4\text{P})[\text{Co(mnt)}_2]$, 1.00×10^{-3} *M*, containing pyridine at the concentrations marked.

Table V. Amine Adduct Solution Spectra[a]

L	Freq, kK (10^{-3} ε)				
		Mono Adducts $[\text{Co(mnt)}_2\text{L}]^-$			
Pyridine	~9 (≤0.1)	14.30 (>2.8)	22-22.5 sh (<4)	27.0-27.2 (≥10)	39.2 (>40)
Imidazole		14.55 (>2)	22-22.5 sh (<4.5)	27.0 sh (>8)	36-37 (>26)
2-Methylimidazole	9.4 (≤0.1)	14.6 (≥2.8)	21.5-22 sh (<3.2)	26.5 (>11)	36.7 (~30)
Morpholine	9.4 (~0.15)	14.45 (≥3.1)	22-22.5 sh (<4)	27.2 (≥12.9)	36.7 (~33)
Piperidine	9.3 (~0.15)	14.5 (~2.9)	22-22.5 sh (<4)	27.0 (~12)	36.7 (~32)
dabco	9.3 (0.15)	14.30 (3.4)	22.0 (5.0)	27.0 (12.5)	
Aniline		~13.9 (≥3.2)	22.0 sh (4.8)	27.2 (12.7)	
		Bis Adducts $[\text{Co(mnt)}_2\text{L}_2]^-$ [c]			
Pyridine	14.55 (0.60	22.8 (4.9)	32.6 (28)		
Imidazole	~15.3 (0.4)	22.5 (5.4)	32.6 (25)	37.7 (36.8)	
Morpholine	16.0 (0.4)	22.75 (5.8)	32.9 (26)	38.0 (40)	
$n\text{-BuNH}_2$		23.0 (4.1)	33.7 (36)	36.8 (35)	
N_2H_4		23.3 (4.2)	34.2 (35)	36.5 (36)	

[a] In acetonitrile, 10^{-3} *M*. [b] sh ≡ shoulder. [c] Concentrated, not neat liquid amines.

which we find no evidence of adduct formation in solution are *N,N*-dimethylaniline, *N,N*-diethylaniline, 2-methylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, *N,N*-dimethylbenzylamine, tri-*n*-propylamine, diisopropylethylamine, *N*-

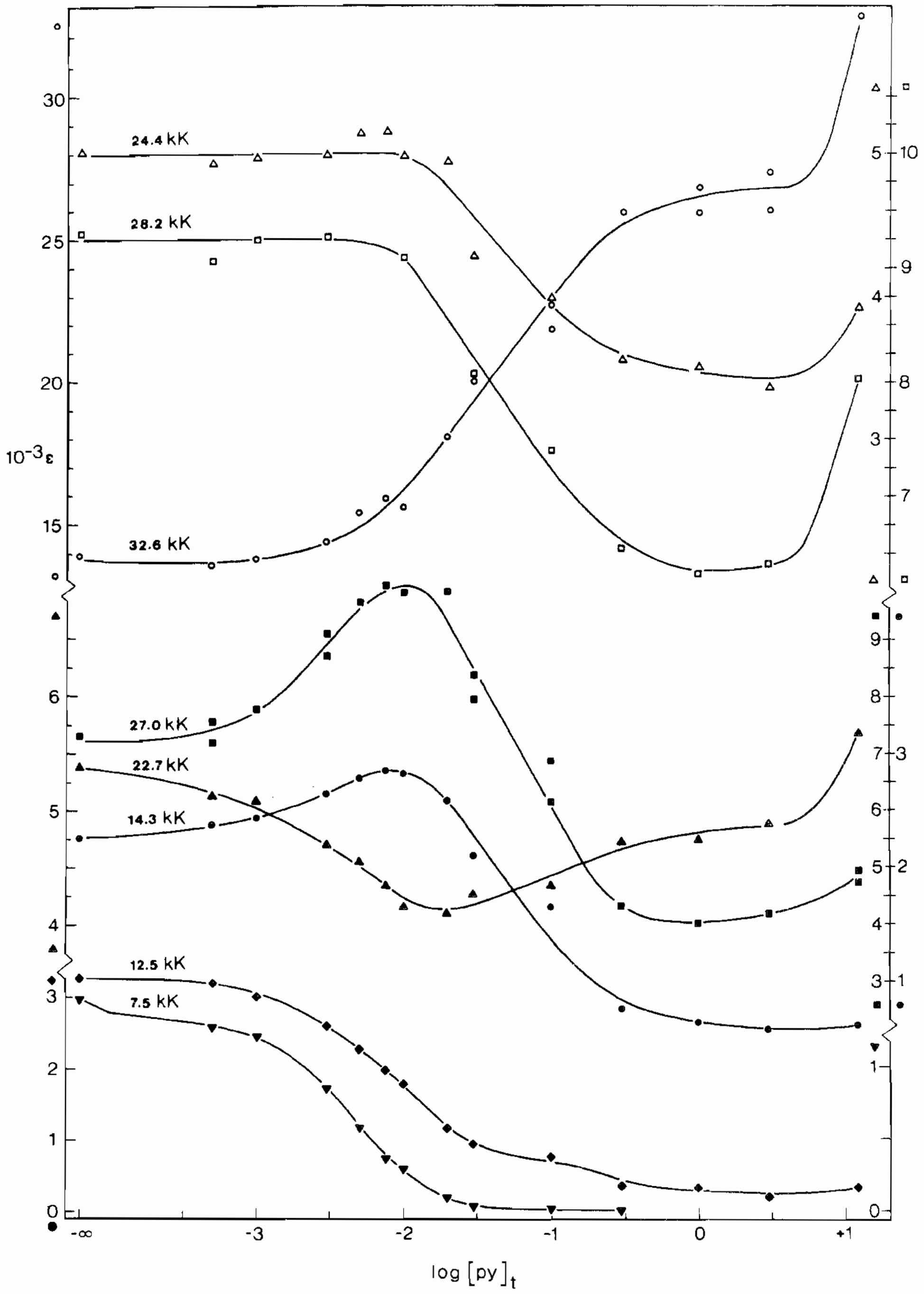


Figure 4. Extinction coefficients at 24.4, 28.2, 32.6, 27.0, 22.7, 14.3, 12.5, and 7.5 kK, plotted against the logarithm of the total added pyridine concentration, for a 1.00×10^{-3} *M* solution of $(Bu_4P)[Co(mnt)_2]$ in acetonitrile. The vertical extinction coefficient scale appropriate for each trace is marked with the symbol of that trace.

methylmorpholine, *N*-ethylmorpholine, triethanolamine, triethanolamine borate, dicyclohexylamine, 2-methylpiperidine, diphenylamine, pyrrole, 2-aminopyridine, and 1,2-diphenylhydrazine.

The formation constants for complexes $[Co(mnt)_2(N\text{-}N)]^-$ with bidentate amines ethylenediamine, 2,2′-dipyridyl, 1,10-phenanthroline, dimethylglyoxime, biacetyl dihydrazone, and biacetyl bisanil are $>10^5$ M^{-1}. In dichloromethane or acetonitrile solution the formation constant of $[Co(tfd)_2(en)]^-$ is high, $>10^5$ M^{-1}, but there are indications of adduct dissociation in the presence of alcohols or water, and the adduct is noticeably solvatochromic.[20]

Crystallization of Adducts of $[Co(mnt)_2]^-$. The adducts crystallized and satisfactorily analyzed are listed with appropriate data in Table I. In crystalline form the mono adducts are dark green, the heterocyclic amine bis adducts are light green, and the primary amine bis adducts are brown. All solid adducts with monodentate amines are to some degree unstable by loss of amine on standing unless kept in closed containers.

For several amines either the mono or the bis adduct can be obtained in high relative concentration in solution by adjustment of total amine concentration, and in some cases two apparently isomeric bis adducts exist in solution, depending on the solvent. However, no more than one type of adduct could be crystallized for any amine. All amine adduct equilibria are rapidly established,[7,21] and the adduct isolated need not be the predominant species in solution.

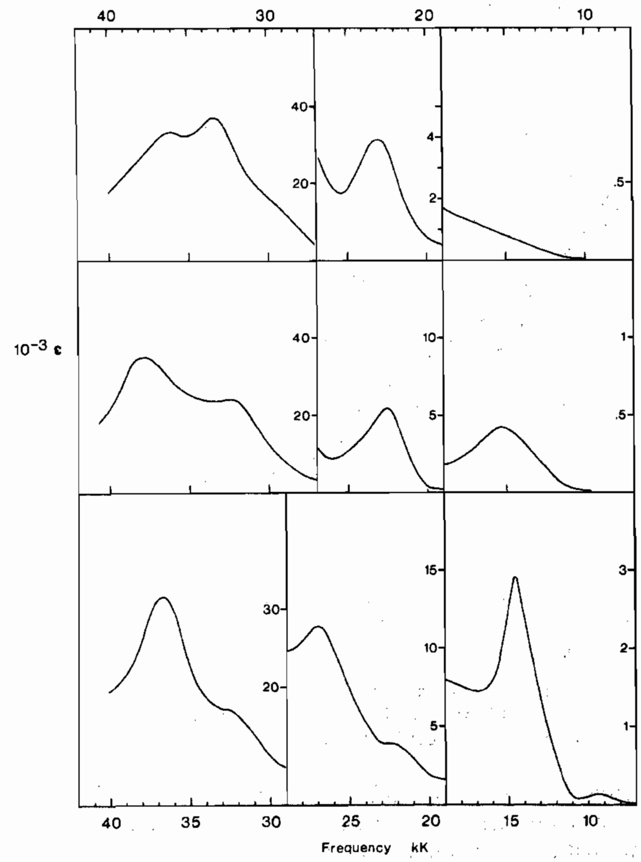


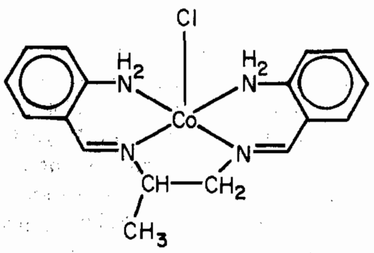
Figure 5. Representative spectra of amine adducts of $[Co(mnt)_2]^-$. Bottom: mono-piperidine adduct spectrum (10^{-3} *M* $[Co(mnt)_2]^-$, 10^{-2} *M* total piperidine). Middle: bis-imidazole adduct spectrum, typical of green bis adducts (10^{-3} *M* $[Co(mnt)_2]^-$, 9.4 × 10^{-2} *M* total imidazole). Top: bis-*n*-butylamine adduct spectrum, typical of brown bis adducts (10^{-3} *M* $[Co(mnt)_2]^-$, 0.2 *M* total *n*-butylamine).

A series of crystallizations in the presence of various concentrations of pyridine, using Bu_4P^+, Bu_4N^+, and $pyMe^+$ salts of $[Co(mnt)_2]_2^{2-}$, have yielded either the parent dimer, the bis adduct, or a mixture of the two, but not the mono adduct $[Co(mnt)_2py]^-$. The mixture of $(cation)_2[Co(mnt)_2]_2$ and $(cation)[Co(mnt)_2(py)_2]$ could be distinguished from $(cation)[Co(mnt)_2py]$ by the variable and nonstoichiometric weight loss on removal of pyridine and by the presence of an absorption maximum at 7.5 kK in the mull spectrum. Similarly, in all other cases where the bis-amine adducts form in solution at moderate amine concentrations the mono adduct could not be crystallized. These results are contrary to the claims of others[3,4] to have isolated the mono adduct with pyridine and pyridine derivatives. No analytical data have been reported to support the isolation of $[Co(mnt)_2py]^-$ salts, and in fact the published analytical data for the adducts with 3- and 4-methylpyridine and 4-vinylpyridine are better fitted to bis adduct formulation.[22] Furthermore, all previously reported adducts of $[Co(mnt)_2]^-$ with pyridine or its derivatives were diamagnetic, whereas the pyridine mono adduct in solution and the crystalline mono adducts with cyclic secondary amines are paramagnetic (see below).

Preparation of $(Bu_4N)_2[(mnt)_2Co(4,4'\text{-dipy})Co(mnt)_2]$ has been claimed,[5] but the diamagnetic compound is reported to absorb at 7.2 kK which again indicates that the preparation could be a mixture containing $[Co(mnt)_2]_2^{2-}$. On reinvestigation of this system we have obtained $[Co(mnt)_2(4,4'\text{-dipy})]_n^{n-}$ (as Bu_4P^+ and Bu_4N^+ salts) as the only pure complex. The mull spectrum is similar to that of $[Co(mnt)_2(py)_2]^-$ and shows no evidence of the 7.5-kK band. It is doubtful whether salts of $[(mnt)_2Co(4,4'\text{-dipy})Co(mnt)_2]^{2-}$ could be isolated[23] should this species be shown to exist in solution.

Ammonia, hydrazine, and phenylhydrazine form tan crystalline adducts, very similar to the bis adducts with primary alkylamines, but analytical characterization has not been possible due to loss of ammonia and reduction of the hydrazine adducts to $[Co(mnt)_2]^{2-}$.

Magnetic susceptibility data for the crystalline compounds are contained in Table IV. Both bis adducts investigated are diamagnetic. A neat pyridine solution, containing only $[Co(mnt)_2(py)_2]^-$, is reported to be diamagnetic. At room temperature the morpholine and piperidine mono adducts are apparently in spin-triplet states, but in view of the fact that related complexes $[Co(tdt)_2]^-$ [24,25] and Co(abpn)Cl (I)[26]



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possess a spin-singlet state with a very low-lying spin-triplet state, we have measured the magnetic susceptibility of $(Bu_4P)[Co(mnt)_2(piperidine)]$ down to liquid nitrogen temperature. The data have been least-squares fitted to a model (A) with only a spin-triplet ground state and a model (B) with both spin-singlet and spin-triplet states available at variable energy, with the triplet-state *g* factor and the *total* temperature-independent susceptibility, χ_{cor} (combined ligand diamagnetism and second-order Zeeman paramagnetism), as adjustable parameters. The results are as follows: for model A, $g = 1.89 \pm 0.02$ ($S = 1$ ground state), $\chi_{cor} = +(220 \pm 120) \times 10^{-6}$ cgsu; for model B, $S = 0$ ground state, $S = 1$ excited state at $+19 \pm 15$ cm^{-1}, $g(S = 1) = 2.30 \pm 0.12$, $\chi_{cor} = -(125 \pm 350) \times 10^{-6}$ cgsu. The data do not extend to temperatures low enough to distinguish unequivocably the two models. However, for model A the low *g* factor and the large (*ca.* $+500 \times 10^{-6}$ cgsu) second-order Zeeman paramagnetism implied in χ_{cor} are unprecedented. It is believed that model B is the correct description, and the low-temperature data necessary for confirmation are being sought.

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[21] I. G. Dance, *Inorg. Chem.*, 12, 2381 (1973).

[22] The found,[4] (calculated for mono adduct), [calculated for bis adduct], percentages are as follows: $(n\text{-}Bu_4N)[Co(mnt)_2]$-3-Me(py): C, 55.7 (53.38) [56.29]; H, 6.4 (6.42) [6.56]; N, 12.7 (12.45) [12.76]; S, 17.0 (19.00) [16.70]. $(n\text{-}Bu_4N)[Co(mnt)_2]$-4-Me(py): C, 56.7 (53.38) [56.29]; H, 6.3 (6.42) [6.56]; N, 12.9 (12.45) [12.76]; S, 17.9 (19.00) [16.70]. $(n\text{-}Bu_4N)[Co(mnt)_2$-4-vinylpyridine: C, 54.6 (54.21) [57.62]; H, 6.2 (6.31) [6.36]; N, 12.1 (12.23) [12.38]; S, 15.8 (18.67) [16.19].

[23] Eaton and Holm's preparation of $(n\text{-}Bu_4N)_2[Co_2(mnt)_4(4,4'\text{-dipy})]$ is reported to melt at 190–191°, a sharpness which could be regarded as a mark of purity, were it not that we find that $(n\text{-}Bu_4N)[Co(mnt)_2(4,4'\text{-dipy})]$ melts at 196–197° and $(n\text{-}Bu_4N)_2[Co(mnt)_2]_2$ melts at 200–200.5°.

[24] tdt ≡ toluene-3,4-dithiolate. R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, *Inorg. Chem.*, 7, 741 (1968).

[25] C. R. Ollis, D. Y. Jeter and W. E. Hatfield, *J. Amer. Chem. Soc.*, 93, 547 (1971).

[26] M. Gerlock, B. M. Higson, and E. D. McKenzie, *Chem. Commun.*, 1149 (1971).

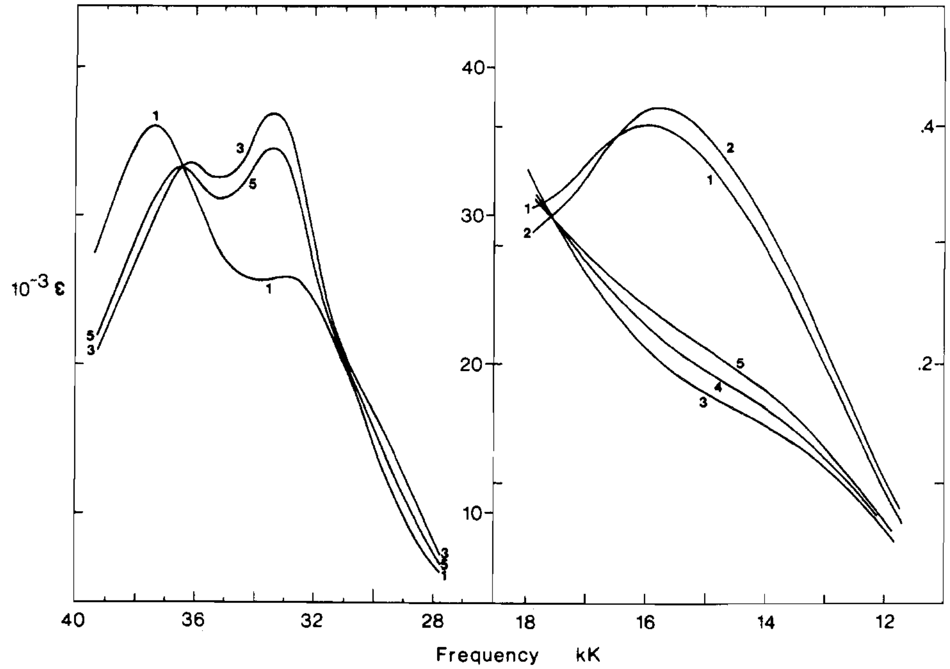

Figure 6. Selected spectral traces for 10^{-3} *M* $(Bu_4P)[Co(mnt)_2(n\text{-butylamine})_2]$ in different liquid media: 1, neat *n*-butylamine; 2, 20% *n*-butylamine–80% benzene; 3, 60% *n*-butylamine–40% acetonitrile; 4, 40% *n*-butylamine–60% acetonitrile; 5, 20% *n*-butylamine–80% acetonitrile (all liquid compositions by volume). The spectrum in 80% *n*-butylamine–20% acetonitrile is almost identical with trace 3.

The paramagnetism of the morpholine and pyridine mono adducts in solution has been demonstrated by nmr. An acetonitrile-d_3 solution containing *ca.* 0.05 *M* $(n\text{-}Bu_4P)[Co(mnt)_2]$, 0.3 *M* morpholine, and 0.1 *M* $n\text{-}Bu_4P^+ClO_4^-$, such that $[Co(mnt)_2(morph)]^-$ is the predominant species, shows the α and β C-H protons shifted (under fast amine-exchange conditions) downfield by 230 and 280 Hz, respectively, from their resonances in the absence of the complex. The N-H proton undergoes a larger upfield shift. The cation protons are not detectably shifted. Incremental addition of $(n\text{-}Bu_4P)[Co(mnt)_2]$ to a solution 0.4 *M* in pyridine causes downfield shifts of all pyridine resonances without appreciable broadening of the multiplets. At 0.1 *M* total cobalt complex, when the solution contains approximately equal concentrations of mono- and bis-pyridine adducts, the downfield shifts from the diamagnetic resonances are as follows: H_α, 300 Hz; H_β, 190 Hz; H_γ, 20 Hz.

Electrochemical investigations of the $Co(mnt)_2$-py adducts are described separately.[21]

Discussion

The data reported here on amine adduct formation and stereochemistry in solution and crystalline states extend and elucidate previous work.[3-7,15] The ordering of formation constants with respect to a wide range of amines is the same for both iron and cobalt dithiolene complexes and is related to the amine Bronsted basicity and steric crowding at nitrogen in the normal manner.[27-31] All tertiary amines except trimethylamine and dabco have no detectable coordinating ability with $[Co(mnt)_2]_2^{2-}$ at room temperature and therefore are suitable for utilization, together with their conjugate acids, as nonaqueous buffers for cobalt (and nickel) dithiolene complexes. The general magnitude of amine adduct formation by $[Co(mnt)_2]_2^{2-}$ in acetonitrile is similar to that known for bis(dipivaloylmethanato)copper(II),[32] vitamin B_{12},[33] and some nickel porphyrins[34] but less than that of bis(diethyl dithiophosphato)nickel(II).[30b,35]

The amine adduct formation constants are dependent on the metal in the dithiolene complex, $K_1(Fe) > K_1(Co)$ $(\gg K_1(Ni))$. For iron and cobalt this is the reverse of the relative magnitudes of the dimer association constants in very poorly coordinating solvents. It has not been possible to determine whether the order of formation constants for the five-coordinate amine adducts is due to stronger amine binding of iron over cobalt or to greater stability of the cobalt complex in dimeric form.

A more intriguing contrast between iron and cobalt dithiolenes arises in the formation of six-coordinate amine adducts, in that $[Co(mnt)_2(amine)]^-$ readily forms $[Co(mnt)_2(amine)_2]^-$ provided there is minimal steric hindrance by the amine, while $[Fe(mnt)_2(amine)]^-$ shows no evidence of further coordination with any monodentate amine; $K_2(Co)/K_1(Co) \gg K_2(Fe)/K_1(Fe)$, at room temperature. This is an unusual result. Although insufficient data are available to attempt a complete thermodynamic explanation, it may be surmised from the electronic structure viewpoint that the highest filled molecular orbitals in six-coordinate $[Co(mnt)_2(amine)_2]$ are lower in energy than analogous orbitals in $[Fe(mnt)_2(amine)_2]^-$ in any stereochemistry. It is noted that the enthalpies of adduct formation are appreciably negative and lower tem-

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peratures increase adduct formation. Therefore our results at ambient temperature are not necessarily contradictory to the assertions of others that solvent adducts of $[Fe(mnt)_2]^-$ are six-coordinate at 77°K[36] and that about 5% of the total iron in a frozen solution of $[Fe(mnt)_2]^-$ in pyridine at 140°K is present in the form of a spin-doublet bis adduct.[6]

The five-coordinate mono adducts ($S = {}^3/_2$, Fe; $S = 1$, Co) are presumably square pyramidal as has been established for mono adducts with other ligands.[13,37] The two spectrally differentiated types of diamagnetic bis-amine adducts $[Co(mnt)_2L_2]^-$ are regarded as stereoisomers. By spectral comparison the green bis adducts are postulated to possess cis-octahedral stereochemistry, while the brown bis adducts may be prismatic or trans octahedral, the latter being the preferred hypothesis. Some factors influencing this stereoisomerism can be recognized. First, only primary amines (and hydrazines) form the brown isomer, and therefore weakly repulsive or very weakly bonding interactions between the amine and the dithiolene chelate ligand probably occur. Second, the stereochemistry with these same amines is dependent upon the solution environment of the bis adduct, and hydrogen bonding interactions between coordinated amine and solvent amine appear to be influential.[38,39] The appreciable solvatochromism of cis-octahedral $[Co(S\text{-}S)_2en]^-$ (S-S ≡ mnt, tfd) also evinces the influence of solute–solvent interactions for these amine adducts. There is no evidence for stereochemical dependence on the electronic structure at amine nitrogen.

The five-coordinate adducts $[Co(mnt)_2(amine)]^-$ show spin-triplet paramagnetism at room temperature, but it is possible that the ground state is actually spin-singlet, with the triplet at *ca.* +20 cm^{-1}. Similar close-lying spin states exist in square-planar $[Co(tdt)_2]^-$.[24,25] It may be reasonably presumed that a five-coordinate adduct $[Co(mnt)_2(DMSO)]^-$ would have two unpaired electrons at room temperature and that any six-coordinate disolvate would be diamagnetic, which leads to the postulate that DMSO solutions[15] of $[Co(mnt)_2]_2{}^{2-}$ contain only the monosolvate.

Finally, we wish to draw attention to some remarkable similarities between mnt complexes and analogs with quadridentate nitrogen ligands, M(abpn) (see I).[40] The electronic spectrum of five-coordinate Co(abpn)Cl is very similar to that of $[Co(mnt)_2(piperidine)]^-$; both complexes show spin-triplet paramagnetism at room temperature, and the former has a spin-singlet ground state.[26] This resemblance extends to the changes observed in the spectrum when Co(abpn)Cl is converted to diamagnetic ClCo(abpn)py. The reported change is essentially the disappearance of intense bands at 13.1 and 26.6 kK, while the conversion of paramagnetic $[Co(mnt)_2(amine)]^-$ to diamagnetic $[Co(mnt)_2(amine)_2]^-$ is attended by the disappearance of intense bands at 14 and 27 kK. Furthermore, the complexes M(abpn) (M = Co, Ni, Cu) undergo one-electron oxidation to produce M(abpn)X at potentials[40] that are almost identical with the potentials for the one-electron oxidation of the respective complexes $[M(mnt)_2]^{2-}$. These magnetic, spectral and electrochemical correspondences surely reflect similar gross electronic structure in orbitals extending over metal and ligands, despite the differences in ligand detail.

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Registry No. $(Bu_4N)_2[Fe(mnt)_2]_2$, 49567-55-7; $(Bu_4P)_2[Fe(mnt)_2]_2$, 49567-56-8; $(Bu_4N)[Fe(mnt)_2(NH_3)]$, 49567-59-1; $(Bu_4N)[Fe(mnt)_2(n\text{-}BuNH_2)]$, 49567-60-4; $(Bu_4N)[Fe(mnt)_2(t\text{-}BuNH_2)]$, 49567-61-5; $(Bu_4N)[Fe(mnt)_2(PhCH_2NH_2)]$, 49567-62-6; $(Bu_4N)[Fe(mnt)_2(piperidine)]$, 49567-63-7; $(Bu_4N)[Fe(mnt)_2(morpholine)]$, 49567-64-8; $(Bu_4N)[Fe(mnt)_2(abn)]$, 49567-65-9; $(Bu_4N)[Fe(mnt)_2(4\text{-}cyanopyridine)]$, 39472-14-5; $(Bu_4N)[Fe(mnt)_2(2\text{-}aminopyridine)]$, 39472-13-4; $(Bu_4N)[Fe(mnt)_2(imidazole)]$, 49567-66-0; $(Bu_4N)[Fe(mnt)_2(1\text{-}methylimidazole)]$, 49613-52-7; $(Bu_4N)[Fe(mnt)_2py]$, 24324-57-0; $(Bu_4N)[Fe(mnt)_2(dabco)_{1/2}]$, 49613-53-8; $(Bu_4P)[Fe(tfd)_2(en)_{1/2}]$, 49567-68-2; $[Fe(mnt)_2(2,6\text{-}dimethylpyridine)]^-$, 49567-69-3; $[Fe(mnt)_2(PhNH_2)]^-$, 49567-70-6; $[Fe(mnt)_2(Et_2NH)]^-$, 49567-71-7; $[Fe(mnt)_2(Pr_3N)]^-$, 49567-72-8; $(Bu_4N)_2[Co(mnt)_2]_2$, 49567-57-9; $(Bu_4P)_2[Co(mnt)_2]_2$, 41004-09-5; $(Bu_4P)[Co(mnt)_2(py)_2]$, 49567-73-9; $(Bu_4N)[Co(mnt)_2(py)_2]$, 49567-74-0; $(Bu_4P)[Co(mnt)_2(piperidine)]$, 49567-75-1; $(Bu_4P)[Co(mnt)_2(morpholine)]$, 49567-76-2; $(Bu_4P)[Co(mnt)_2(abn)]$, 49567-77-3; $(Bu_4P)[Co(mnt)_2(PhCH_2NH_2)_2]$, 49567-48-8; $(Bu_4P)[Co(mnt)_2(BuNH_2)_2]$, 49613-48-1; $(Bu_4N)[Co(mnt)_2(BuNH_2)_2]$, 49567-35-3; $(Bu_4P)[Co(mnt)_2(imidazole)_2]$, 49613-49-2; $(Bu_4P)[Co(mnt)_2(1\text{-}methylimidazole)]$, 49567-36-4; $(Bu_4N)[Co(mnt)_2(4,4'\text{-}bipy)]$, 49567-37-5; $[Co(mnt)_2py]^-$, 41004-10-8; $[Co(mnt)_2(imidazole)]^-$, 49567-38-6; $[Co(mnt)_2(2\text{-}methylimidazole)]^-$, 49672-66-4; $[Co(mnt)_2(4\text{-}CNpy)]^-$, 39472-12-3; $[Co(mnt)_2(PhNH_2)]^-$, 49567-39-7; $[Co(mnt)_2(Et_2NH)]^-$, 49567-40-0; $[Co(mnt)_2(dabco)]^-$, 49567-41-1; $[Co(mnt)_2(morpholine)_2]^-$, 49567-42-2; $[Co(mnt)_2(dabco)_2]^-$, 49567-43-3; $[Co(mnt)_2(N_2H_4)_2]^-$, 49567-44-4; $[Co(mnt)_2(2\text{-}methylimidazole)_2]^-$, 49567-45-5; $(Bu_4N)_2[Co(tfd)_2]_2$, 49567-46-6; $(Bu_4N)_2[Fe(tfd)_2]_2$, 19555-30-7; Na_2mnt, 18820-77-4; py, 110-86-1; $PhNH_2$, 62-53-3.

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