It is interesting to compare the Fe–O and Fe–N stretching frequencies of FeQ_3 to those of $FeQ_2 \cdot 2H_2O$. The Fe–O and Fe–N stretching bands of FeQ_3 are higher by 36 and 60 cm^{-1}, respectively, than those of $FeQ_2 \cdot 2H_2O$. Thus the higher the oxidation state, the higher the Fe–O and Fe–N stretching frequencies. The same trend seems to hold between CoQ_3[15] and $CoQ_2 \cdot 2H_2O$.

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Bridged Binuclear Bis-Dithiolene Complexes of Iron and Cobalt

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An extensive series of bridged binuclear bis-dithiolene complexes of iron and cobalt, $(R_4C_4S_4)M{-}(L\text{-}L){-}M(S_4C_4R_4)^z$, with $z = 2-$, R = CN, CF_3, and $z = 0$, R = CF_3, have been prepared by reaction of the bidentate bridging ligand L-L with the appropriate dimeric dithiolene. The bridging ligands contain nitrogen or phosphorus donor atoms. Magnetic moments of the binuclear complexes are consistent with those of analogous mononuclear five-coordinate adducts reported earlier. Cobalt complexes with R = CF_3, $z = 0, 2-$, and L-L = 1,4-bis(diphenylphosphino)benzene, bis(diphenylphosphino)acetylene (DPPA), or *trans*-1,2-bis(diphenylphosphino)ethylene (DPPE) were studied in the most detail. Polarography in dichloromethane reveals a three-member electron-transfer series ($z = 2-, 1-, 0$). Half-wave potentials for the two redox processes of the bridged complexes and the $1- \rightleftharpoons 0$ process of the mononuclear triphenylphosphine analog occur in a range of only 0.2 V, indicating that in the former the cobalt–dithiolene units behave as essentially independent sites in electron-transfer reactions. Mononuclear adducts of L-L formed in the presence of excess bridging ligand were detected by polarography and epr. Solutions containing equimolar amounts of neutral and dianionic complexes with L = DPPA and DPPE were found to exhibit electronic absorption bands at 6850 and 7350 cm^{-1}, respectively, which are attributed to intramolecular electron transfer in the monoanion.

Introduction

The chemistry of bis-dithiolene complexes of transition metals is characterized by the existence of electron-transfer series, which in several cases include members with overall charge z of $2-$, $1-$, and 0.[2] Although in a number of instances the monomeric species have been shown to have a planar four-coordinate structure, some metal dithiolene systems, particularly those of iron and cobalt, readily form five-coordinate dimers,[2-4] five-[2,3-10] and six-coordinate[2,5,8,11,12] base adducts, and tris complexes.[13] Of particular interest in the present study are the species containing five-coordinate base adducts, for which the available structural data reveal a square-pyramidal coordination unit.[9]

In the course of investigating the syntheses and properties of transition metal complexes in which the metals are linked by an unsaturated bridge L-L, we have prepared a series of dithiolene complexes of the general type $(R_4C_4S_4)M{-}(L\text{-}L){-}M(S_4C_4R_4)^z$ with M = Fe, Co, R = CF_3, CN,[14] and $z = 2-, 0$. The following bidentate bridging groups have been employed: pyrazine (pyz), 4,4′-bipyridyl (4,4′-bipy), 4,4′-dipyridyl disulfide (pySSpy), *trans*-1,2-di(4-pyridyl)ethylene (pyC_2H_2py), 1,2-di(4-pyridyl)ethane (pyC_2H_4py), 1,4-bis(diphenylphosphino)benzene (DPPB), *trans*-1,2-bis-(diphenylphosphino)ethylene (DPPE), and bis(diphenylphosphino)acetylene (DPPA). These groups have been selected according to their potential or demonstrated ability to bridge two metal centers in discrete dimers or polymers and because certain of their monodentate analogs (*e.g.*, pyridine, triphenylphosphine) have been shown to form five-coordinate adducts with iron and cobalt dithiolenes.[2,5-9] A number of bi- and polynuclear pyz complexes have been prepared,[15,16] and X-ray diffraction[17] has confirmed the ability of pyrazine ligands to function as a bridge. The known 4,4′-bipy complexes are polymeric.[18] Bridged struc-

(1) NDEA Predoctoral Fellow, 1968–present.

(2) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

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

(4) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *ibid.*, **90**, 4253 (1968).

(5) (a) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *ibid.*, **86**, 2958 (1964); (b) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966); (c) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966).

(6) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4604 (1966).

(7) A. L. Balch, *Inorg. Chem.*, **6**, 2158 (1967).

(8) (a) J. A. McCleverty, N. M. Atherton, N. G. Connelly, and C. J. Winscom, *J. Chem. Soc. A*, 2242 (1969); (b) J. A. McCleverty and B. Ratcliff, *ibid.*, *A*, 1631 (1970).

(9) E. F. Epstein, I. Bernal, and A. L. Balch, *Chem. Commun.*, 136 (1970).

(10) R. W. Johnson, W. R. Muir, and D. A. Sweigart, *ibid.*, 643 (1970).

(11) G. P. Khare, C. G. Pierpont, and R. Eisenberg, *ibid.*, 1692 (1968).

(12) V. P. Mayweg and G. N. Schrauzer, *ibid.*, 640 (1966).

(13) J. A. McCleverty, J. Locke, and E. J. Wharton, *J. Chem. Soc. A*, 816 (1968); E. J. Wharton and J. A. McCleverty, *ibid.*, *A*, 2258 (1969); E. I. Stiefel, L. E. Bennett, Z. Dori, T. H. Crawford, C. Simo, and H. B. Gray, *Inorg. Chem.*, **9**, 281 (1970).

(14) The following abbreviations are used throughout: tfd, $(CF_3)_2C_2S_2$; mnt, $(CN)_2C_2S_2$.

(15) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *Nature (London)*, **189**, 58 (1961); *J. Chem. Soc.*, 1235 (1962); 3156, 5042 (1963).

(16) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).

(17) F. D. Ayres, P. Pauling, and G. B. Robertson, *Inorg. Chem.*, **3**, 1303 (1964); R. G. Vranka and E. L. Amma, *ibid.*, **5**, 1020 (1966); A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Crystallogr., Sect. B*, **26**, 979 (1970).

(18) (a) J. H. Wang and W. S. Brinigar, *Proc. Nat. Acad. Sci. U. S.*, **46**, 958 (1960); (b) J. R. Ferraro and K. C. Davis, *Inorg. Chim. Acta*, **3**, 685 (1969).

TABLE I

CHARACTERIZATION DATA FOR $(R_4C_4S_4)M\text{-}(L\text{-}L)\text{-}M(S_4C_4R_4)^z$ COMPLEXES

						% calcd				% found			
No.	M	R	L-L	z[a]	Mp,[f] °C	C	H	N	F (S)	C	H	N	F (S)
1	Fe[d]	CN	pyz	2−	198–199	50.47	6.19	13.58	(20.73)	50.32	6.14	13.62	(20.47)
2	Fe[e]	CN	4,4′-bipy	2−	196–197	53.03	6.14	12.80	(19.53)	52.98	6.26	12.69	(19.23)
3	Fe[e]	CN	pySSpy	2−	233–234	50.55	5.85	12.20	...	50.38	5.73	12.35	...
4	Fe[e]	CN	pyC_2H_2py	2−	264	53.80	6.17	12.55	...	54.09	6.25	12.68	...
5	Fe[e]	CN	pyC_2H_4py	2−	262	53.72	6.31	12.53	...	53.83	6.30	12.64	...
6	Fe[g]	CN	DPPB	2−	235–236	58.41	6.03	8.73	...	58.65	6.03	8.68	...
7	Fe[e]	CF_3	pyz	2−	184–185	39.49	4.84	3.54	(16.22)[b]	39.56	4.80	3.54	(16.36)[b]
8	Fe[h]	CF_3	4,4′-bipy	2−	169–170	42.03	4.86	3.38	(15.47)[c]	42.14	4.77	3.56	(15.63)[c]
9	Fe[d]	CF_3	DPPB	2−	156–157	48.10	4.97	1.44	...	48.12	5.00	1.34	....
10	Fe[g]	CF_3	DPPB	0	185	37.77	1.65	...	31.17	38.34	1.72	...	33.04
11	Fe[d]	CF_3	DPPE	2−	162	46.84	4.99	1.48	24.03	46.82	4.84	1.58	23.99
12	Fe[g]	CF_3	DPPE	0	209–210	35.71	1.57	...	32.28	35.55	1.47	...	32.55
13	Fe[d]	CF_3	$(DPPA)_2$	0	164–165	45.25	2.23	...	(14.21)[l]	45.13	2.22	...	(14.11)[l]
14	Co[d]	CN	4,4′-bipy	2−	190–191	52.79	6.11	12.74	(19.44)	52.94	6.10	12.64	(19.53)
15	Co[g]	CN	pySSpy	2−	203–205	50.34	5.83	12.15	(23.17)	50.56	6.30	12.02	(23.35)
16	Co[i]	CN	pyC_2H_2py	*j*	194–196	56.60	6.07	12.83	...	56.77	6.09	12.88	. .
17	Co[g]	CN	pyC_2H_4py	*j*	181–184	56.45	6.32	12.80	...	56.55	6.35	12.73	...
18	Co[d]	CN	DPPB	2−	237–238	58.19	6.01	8.70	...	57.86	6.10	8.82	...
19	Co[d]	CF_3	DPPB	0	209	37.61	1.65	...	(17.46)[m]	37.56	1.83	...	(17.75)[m]
20	Co[k]	CF_3	DPPB	2−	199–200	47.95	4.95	1.43	(13.13)	48.08	5.06	1.47	(13.06)
21	Co[d]	CF_3	DPPE	0	227	35.55	1.56	...	(18.08)[n]	35.74	1.83	...	(17.86)[n]
22	Co[d]	CF_3	DPPE	2−	200–201	46.69	4.98	1.47	...	46.50	4.87	1.38	....
23	Co[d]	CF_3	DPPA	0	231	35.60	1.42	...	32.18	35.40	1.44	...	31.93
24	Co[d]	CF_3	DPPA	2−	211	46.73	4.88	1.47	...	47.07	4.94	1.60	...

[a] z = 2− complexes isolated as $(n\text{-}C_4H_9)_4N^+$ salts. [b] Per cent F: calcd, 28.83; found, 29.04. [c] Per cent F: calcd, 27.51; found, 27.95. [d] Brown. [e] Red-brown. [f] Corrected; determined in evacuated sealed tubes. [g] Green. [h] Orange-brown. [i] Olive green. [j] Apparently polymeric with repeating unit $(R_4C_4S_4)M\text{-}(L\text{-}L)^-$. [k] Yellow-brown. [l] Per cent F: calcd, 25.26; found, 26.52. [m] Per cent F: calcd, 31.04; found, 26.80. [n] Per cent F: calcd, 32.13; found, 32.12.

tures have been postulated for binuclear complexes of pyC_2H_2py and pyC_2H_4py,[19] and the binary copolymers of 4,4′-bipy, pyC_2H_2py, and pyC_2H_4py with heme may contain a similar structural unit.[18a] Binuclear complexes with DPPE[20] and DPPA[20-22] bridges have been synthesized. A considerable variety of binuclear DPPA-bridged species are known which contain one to four bridging ligands.[21] The structure of a complex containing a single DPPA bridge has been reported.[22] Some of the references just cited describe isolation of complexes in which only one of the donor atoms of the ligand is coordinated. No metal complexes of pySSpy and DPPB appear to have been prepared prior to this work. This paper describes the preparation of a series of bridged binuclear iron and cobalt dithiolene complexes and the electron-transfer chemistry of certain of these species.

Experimental Section

Preparation of Compounds.—DPPB,[23] DPPE,[24] and DPPA[21b] were prepared by previously published methods. Other bridging ligands were commercially available. $[M(tfd)_2]_2$ and salts of $[M(tfd)_2]_2^-$, $[M(tfd)_2]_2^{2-}$, and $[M(mnt)_2]_2^{2-}$ (M = Fe, Co) were obtained by procedures described elsewhere[3] or given below.

$\mathbf{((\textit{n}\text{-}C_4H_9)_4N)_2[Fe(mnt)_2]_2}$.—A procedure analogous to that used to prepare $((n\text{-}C_4H_9)_4N)_2[Ni(mnt)_2]$[25] was found to yield the desired compound more readily than the reported method.[3] Ferric chloride hexahydrate (27 g, 0.10 mol) dissolved in 150 ml of water was added dropwise to a solution of 41 g (0.22 mol) of Na_2mnt[25] in 600 ml of 50% aqueous ethanol. The reaction mixture was filtered and 74 g (0.23 mol) of tetra-*n*-butylammonium bromide in 250 ml of ethanol was added dropwise. The resultant black solid was collected by filtration, washed with water and then 50% aqueous ethanol, and recrystallized twice from acetone–2-propanol to afford 24 g (42%) of black crystals; mp 197–198°; lit.[3] mp 197–198°.

$\mathbf{((\textit{n}\text{-}C_4H_9)_4N)_2[Co(mnt)_2]_2}$.—The published procedure[26] was impractical for large-scale synthesis. Under a nitrogen atmosphere 100-ml portions of hot dimethyl sulfoxide solutions of cobaltous chloride hexahydrate (11.9 g, 0.050 mol), Na_2mnt[25] (20.5 g, 0.11 mol), and tetra-*n*-butylammonium bromide (37.0 g, 0.115 mol) were mixed and filtered. A solution of iodine (20 g, 0.080 mol) in 40 ml of dimethyl sulfoxide was added; the mixture was stirred for 1–2 min and then poured into 1050 ml of 95% ethanol. After cooling overnight the crystalline product was filtered and washed with 95% ethanol, ether, and *n*-pentane to give 23.6 g (81%) of salt; mp 200–200.5°; lit.[26] mp 198–199°.

Bridged Dithiolene Complexes.—Preparation of $(R_4C_4S_4)M\text{-}(L\text{-}L)\text{-}M(S_4C_4R_4)^z$ species was carried out by mixing solutions of the parent dimeric dithiolene with charge z and *excess* bridging ligand, followed by the addition of a higher boiling solvent to give a solvent medium such that upon partial evaporation the complex precipitated and the unreacted ligand remained in solution. Reactions involving diphosphines were carried out under nitrogen to avoid formation of phosphine oxide complexes,[9] and reactions employing dithiolenes with z = 0 were performed in solvents dried over P_2O_5 or calcium hydride. Tetra-*n*-butylammonium salts of anionic dithiolenes were used in all reactions. Preparation information (per cent excess ligand, solvent medium, per cent yield) is provided in the following summary, the order of which follows the listing of compounds in Table I. Yield data refer to purified products. Recrystallization was generally carried out

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[19] M. Brierley and W. J. Geary, *J. Chem. Soc. A*, 963 (1967).

[20] R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969); R. B. King and A. Efraty, *ibid.*, **8**, 2374 (1969).

[21] (a) A. J. Carty and T. W. Ng, *Chem. Commun.*, 149 (1970); (b) A. J. Carty and A. Efraty, *Inorg. Chem.*, **8**, 543 (1969); (c) A. J. Carty, A. Efraty, T. W. Ng, and and T. Birchall, *ibid.*, **9**, 1263 (1970), and references therein.

[22] A. J. Carty, T. W. Ng, W. Carter, G. J. Palenik, and T. Birchall, *Chem. Commun.*, 1101 (1969).

[23] D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).

[24] A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

[25] A. Davison and R. H. Holm, *Inorg. Syn.*, **10**, 8 (1967).

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

under the same solvent and excess ligand conditions used in the initial isolation. A detailed procedure for a typical preparation follows the summary.

Fe–mnt series: **1**, 1000, 5:4:1 v/v acetone–2-propanol–water (A), 70; **2**, 10, A, 90; **3**, 10, A, 85; **4**, 10, A, 88; **5**, 10, A, 88; **6**, 30, acetone–dichloromethane, 62.[27] Fe–tfd series: **7**, 1000, acetone–2-propanol (B), 84; **8**, 10, B, 94; **9**, 100, acetone–benzene–ethanol, 89;[28] **10**, 30, dichloromethane (C), 74; **11**, 280, dichloromethane–toluene (D), 78; **12**, 10, C, 76; **13**, 11, D, 73. Co–mnt series: **14**, 10, A, 97; **15**, 10, A, 86; **16**, 10, acetone–DMF (E), 69;[29] **17**, 10, E, 100;[29] **18**, 30, acetone–benzene, 99. Co–tfd series: **19**, 14, D, 18;[30] **20**, 50, D, 80; **21**, 26, D, 75; **22**, 60, D, 83; **23**, 60, dichloromethane–toluene–heptane, 60; **24**, 43, D, 79.

$((n\text{-}C_4H_9)_4N)_2[(tfd)_2Co\text{-}DPPE\text{-}Co(tfd)_2]$.—Under a nitrogen atmosphere solid DPPE (63 mg, 0.16 mmol) was added to 150 mg (0.10 mmol) of $((n\text{-}C_4H_9)_4N)_2[Co(tfd)_2]_2$ dissolved in 125 ml of dichloromethane. Toluene (100 ml) was added and the volume of the hot solution was reduced until solid formed. After cooling overnight, the crystalline product was collected by filtration and recrystallized from dichloromethane–toluene containing 10 mg of DPPE to yield 157 mg (83%) of brown crystals, mp 200–201°.

$(tfd)_2Fe\text{-}DPPB\text{-}Fe(tfd)_2$.—The only exception to the usual synthetic procedure was the preparation of this compound, which was carried out by a reaction analogous to that reported between $((C_2H_5)_4N)[Fe(tfd)_2]_2$ and triphenylarsine.[7] A mixture of 0.445 g (0.388 mmol) of $((C_2H_5)_4N)[Fe(tfd)_2]_2$[3] and 0.114 g (0.256 mmol) of DPPB in 50 ml of dry dichloromethane was stirred overnight under a nitrogen atmosphere. $((C_2H_5)_4N)_2[Fe(tfd)_2]_2$[31] (0.19 g, 0.15 mmol) was removed by filtration and the green filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane–pentane to yield 0.209 g (74%) of product whose elemental analysis (*cf.* Table I) supports the binuclear bridged formulation but indicates that the compound was not obtained in a highly pure state. The infrared spectrum was almost identical with that of the cobalt analog.

$((n\text{-}C_4H_9)_4N)[Fe(mnt)_2py]$.—Preparation of this compound has been claimed by McCleverty, *et al.*,[8a] but the analytical data given are inconsistent with the stated stoichiometry. The compound was obtained by reaction of a 25-fold excess of pyridine with $((n\text{-}C_4H_9)_4N)_2[Fe(mnt)_2]_2$ in 5:4:1 acetone–2-propanol–water solvent mixture. An 88% yield of red-brown crystalline product was obtained; mp 170–171°; lit.[8a] mp 130° dec. *Anal.* Calcd for $C_{29}H_{41}N_6S_4Fe$: C, 52.95; H, 6.28; N, 12.78. Found: C, 53.29; H, 6.29; N, 12.87.

$((n\text{-}C_4H_9)_4N)[Fe(tfd)_2py]$.—This compound was obtained in 80% yield from $((n\text{-}C_4H_9)_4N)_2[Fe(tfd)_2]_2$ and an eightfold excess of pyridine using the same solvent medium as in the preceding preparation; red-brown crystals were formed; mp 136°. *Anal.* Calcd for $C_{29}H_{41}F_{12}N_2S_4Fe$: C, 41.98; H, 4.98; N, 3.38. Found: C, 42.10; H, 5.07; N, 3.55.

Other Reactions.—Reaction of $[M(tfd)_2]_2$ (M = Fe, Co) with 4,4′-bipy in dry dichloromethane under nitrogen resulted in formation of brown insoluble powders. Similarly, reaction of $[Co(tfd)_2]_2$ with a pyz in dry *n*-pentane gave a brown insoluble material. These products did not melt below ~300° and are presumably polymeric. They were not further characterized.

Infrared Spectra.—Spectra in the 4000–1300- and 1300–400-cm^{-1} ranges were recorded as Kel-F and Nujol mulls, respectively, using a Perkin-Elmer 337 grating spectrometer. The principal use of the infrared data was to provide evidence, based on nearly identical spectra, that species of the type $(R_4C_4S_4)M\text{-}(L\text{-}L)\text{-}M(S_4C_4R_4)^z$ have the same or closely analogous structures in the solid state for a given z and M = Fe and Co. The following ir data for the DPPB series of tfd complexes are provided to demonstrate the spectral similarities found.

$(tfd)_2M\text{-}DPPB\text{-}M(tfd)_2$: M = Fe: 3090 (w), 3070 (w), 1440 (s), 1435 (s), 1425 (s), 1374 (w), 1360 (w), 1350 (m), 1266 (s), 1219 (s), 1192 (s), 1144 (s), 1105 (w), 1089 (m), 931 (m), 851 (m), 744 (m), 735 (m), 723 (s), 697 (sh), 690 (s), 684 (s), 610 (w), 546 (s), 534 (s), 491 (s), 472 (w), 460 (m), 440 (w), 427 cm^{-1} (m). M = Co: 3060 (w), 1470 (m), 1450 (m), 1425 (s), 1421 (s), 1365 (w), 1355 (m), 1330 (w), 1258 (s), 1221 (s), 1187 (s), 1142 (s), 1104 (m), 1088 (m), 921 (m), 848 (m), 745 (m), 737 (m), 722 (s), 699 (m), 690 (s), 683 (s), 613 (w), 544 (s), 537 (s), 491 (s), 476 (w), 456 (w), 438 (w), 423 cm^{-1} (s).

$((n\text{-}C_4H_9)_4N)_2[(tfd)_2M\text{-}DPPB\text{-}M(tfd)_2]$: M = Fe: 3060 (w), 2960, (s), 2940 (m), 2870 (m), 1530 (m), 1480 (s), 1460 (m), 1430 (s), 1379 (m), 1254 (sh), 1239 (s), 1227 (s), 1172 (s), 1163 (s), 1154 (s), 1130 (s), 1088 (m), 1071 (w), 1027 (w), 1015 (w), 999 (w), 909 (m), 892 (m), 875 (m), 840 (m), 748 (s), 744 (s), 716 (s), 690 (s), 613 (w), 549 (s), 527 (s), 495 (m), 474 (w), 437 (m), 429 cm^{-1} (m). M = Co: 3050 (w), 2960 (s), 2920 (m), 2860 (m), 1510 (s), 1470 (s), 1445 (m), 1420 (s), 1365 (m), 1255 (sh), 1242 (s), 1232 (s), 1172 (sh), 1164 (s), 1155 (s), 1131 (s), 1088 (m), 1071 (w), 1024 (w), 1012 (w), 997 (w), 907 (m), 874 (w), 837 (m), 748 (m), 743 (m), 716 (s), 689 (s), 612 (w), 550 (s), 530 (s), 497 (m), 475 (w), 440 (w), 431 cm^{-1} (w).

Other Physical Measurements.—Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Magnetic susceptibilities were measured by the Gouy or Faraday method with $HgCo(NCS)_4$ as the calibrant. Epr measurements were made on a Varian V-4502 spectrometer. Polarographic data were obtained in dichloromethane solution with a rotating platinum electrode using a modified ORNL Model 1988 polarograph equipped with a three-electrode configuration. The cell and reference electrode described elsewhere[3] were used, with 0.50 *M* tetra-*n*-butylammonium perchlorate as supporting electrolyte.

Results and Discussion

Dimeric iron and cobalt dithiolene complexes have been shown in a previous investigation[3] to display the electron-transfer series (1) and to form five-coordinate base adducts (2).[2,5–9] All four members of the series (1) have been detected for tfd complexes, and in

$$2[MS_4]^{2-} \rightleftharpoons [MS_4]_2{}^{2-} \rightleftharpoons [MS_4]_2{}^{-} \rightleftharpoons [MS_4]_2 \qquad (1)$$

$$[MS_4]_2{}^{z} + 2L \rightleftharpoons 2[L(MS_4)]^{z/2} \qquad (2)$$

the cobalt–tfd system all four have been isolated.[3,31] A large number of five-coordinate complexes formed with bases such as pyridine and tertiary phosphines, as indicated by reaction 2 in which z = 2− or 0, have been isolated and their spectral and magnetic properties determined.[5–8] Polarographic studies suggest the electron-transfer series (3), in which the (z = 1−) ⇌ (z = 0) step is the most clearly demonstrated.[7,8] In series (1) and (3) the half-wave potentials follow the usual order; *viz.*, $E_{1/2}$(tfd) is less positive than $E_{1/2}$(mnt)

$$L(MS_4)^{2-} \rightleftharpoons L(MS_4)^{-} \rightleftharpoons L(MS_4)^{0} \rightleftharpoons L(MS_4)^{+} \qquad (3)$$

for a given oxidation step involving complexes of the same metal.[2] In view of the results obtained for the monoadducts it was considered of value to prepare and study several series of bridged binuclear com-

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(27) The complex was precipitated by cooling a mixture of hot dichloromethane solutions of the reactants and was recrystallized from hot acetone containing 10% excess DPPB followed by washing with dichloromethane.

(28) DPPB (2.4 mmol) dissolved in 50 ml of benzene was added to 0.69 mmol of $((n\text{-}C_4H_9)_4N)_2[Fe(tfd)_2]_2$ in 50 ml of acetone, the volume was reduced to ~30 ml, and the solution was filtered. Addition of 10 ml of ethanol to the hot filtrate followed by cooling (~5°) for 2 days gave large red-brown crystals which were dried under vacuum at ~80°.

(29) The reagents were mixed in acetone solution (10% excess ligand for 2:1 stoichiometry), and the precipitate which formed immediately was recrystallized from DMF containing 10% excess ligand. About 50% of the initial dithiolene complex was recovered from the acetone filtrate.

(30) The product was recrystallized several times from dichloromethane and/or toluene, in which it is very soluble.

(31) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

plexes $(S_4M)\text{-}(L\text{-}L)\text{-}(MS_4)^z$ derived from tfd and mnt and a variety of bridging bidentate ligands L-L. Properties of interest include the electron-transfer reactions and interactions of the two metal centers across the intervening bridge.

Synthesis and Characterization.—The bridged complexes were prepared by reaction of the appropriate iron or cobalt dithiolene dimer $[MS_4]_2^z$ (z = 0, 2−) with the bridging ligand. The reaction is, in effect, one of ligand insertion as represented by (4). Because the reaction mechanism has not been investigated, it can only be postulated that the reaction proceeds in stages

$$[MS_4]_2^z + L\text{-}L \rightleftharpoons (S_4M)\text{-}(L\text{-}L)\text{-}(MS_4)^z \qquad (4)$$

such as those represented by reactions 5–7 or an analogous set involving ligand attack on the intact dimer. The limited data available indicate that the actual equilibria may be more complicated than (5)–(7). Isolation of the binuclear complexes was accomplished

$$[MS_4]_2^z \rightleftharpoons 2MS_4^{z/2} \qquad (5)$$

$$MS_4^{z/2} + L\text{-}L \rightleftharpoons (MS_4)(L\text{-}L)^{z/2} \qquad (6)$$

$$MS_4^{z/2} + (MS_4)(L\text{-}L)^{z/2} \rightleftharpoons (S_4M)\text{-}(L\text{-}L)\text{-}(MS_4)^z \qquad (7)$$

by choice of solvent media and (L-L):$[MS_4]_2^z$ mole ratio such that upon partial evaporation the desired species precipitated. The complexes prepared are listed in Table I. Only dianionic cobalt– and iron–mnt species were prepared owing to the inaccessibility of $[M(mnt)_2]_2$. Both neutral and dianionic cobalt– and iron–tfd complexes could be obtained by use of $[M(tfd)_2]_2$ and $((n\text{-}C_4H_9)_4N)_4[M(tfd)_2]_2$, respectively. Pairs of complexes with z = 2−, 0 were isolated with (L-L) = DPPB, DPPE (M = Fe, Co), and DPPA (M = Co).

Reaction of DPPB with $[Fe(tfd)_2]_2^-$ did not yield $(tfd)_2Fe\text{–}DPPB\text{–}Fe(tfd)_2^-$. Instead the reaction proceeded according to (8), which is analogous to Balch's preparation[7] of $Fe(tfd)_2(As(C_6H_5)_3)$ from the same starting complex.

$$2[Fe(tfd)_2]_2^- + DPPB \rightleftharpoons (tfd)_2Fe\text{–}DPPB\text{–}Fe(tfd)_2 + [Fe(tfd)_2]_2^{2-} \qquad (8)$$

In only three cases did the analytically characterized reaction products not possess properties consistent with discrete monobridged binuclear complexes. The systems pyC_2H_2py- and $pyC_2H_4py\text{–}[Co(mnt)_2]_2^{2-}$ afforded products with the stoichiometry $[(mnt)_2Co(L\text{-}L)]_n^-$. $[Fe(tfd)_2]_2$ and DPPA in 1:1 stoichiometry yielded $Fe_2(tfd)_4(DPPA)_2$, which may contain two cis-octahedral doubly bridged units. In each of these cases the electronic spectra were distinctly different from the spectra of related five-coordinate complexes. The absorption at ~7200 cm^{-1} in $(mnt)_2Co\text{–}bipy\text{–}Co(mnt)_2^{2-}$ is absent in the spectra of $[(mnt)_2Co(L\text{-}L)]_n^-$ species, whose lowest energy band occurs at ~14,800 cm^{-1}, similar to that of $(mnt)_2Co(2,2'\text{-}bipy)^{2-}$.[8] The pyC_2H_2py and pyC_2H_4py complexes are presumably polymeric, but a cis-octahedral doubly bridged structure cannot be excluded, particularly for the more flexible pyC_2H_4py complex. The lowest energy band of $Fe_2(tfd)_4(DPPA)_2$ occurs at 5920 cm^{-1}, whereas the lowest energy absorptions of $(tfd)_2Fe\text{–}(L\text{-}L)\text{–}Fe(tfd)_2$, (L-L) = DPPB or DPPE, are near 16,000 cm^{-1}. For the other complexes in Table I the electronic spectra of each group derived from the same dithiolene dimer and containing the same L-L donor atoms are very similar. Infrared spectra of complexes differing only in metal were nearly identical in most cases, with only minor shifts in band positions observed. This is taken to indicate similar structures in the solid state. Representative comparisons are given in the Experimental Section. Schematic structures proposed for the bridged binuclear complexes and mononuclear adducts with L-L, based on the reported structures of dithiolene adducts,[9] are set out in Figure 1. Spectra of pyz complexes did not contain medium to strong bands in the region attributed to absorption by monodentate pyrazine.[15]

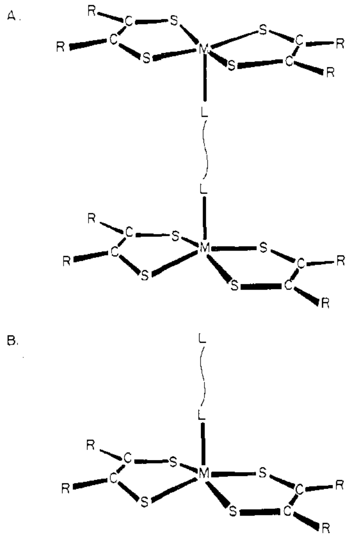

Figure 1.—Structures proposed for bridged binuclear complexes $(R_4C_4S_4)M\text{–}(L\text{-}L)\text{–}M(S_4C_4R_4)^z$ (A) and mononuclear adducts $(R_4C_4S_4)M\text{–}(L\text{-}L)^{z/2}$ (B) formed in the presence of excess bridging ligand.

Polarographic Studies.—In order to investigate the electron-transfer reactions of bridged complexes, polarographic measurements were performed on several series of iron– and cobalt–tfd species containing diphosphine bridging groups. These complexes were selected because they could be prepared in two oxidation levels (z = 2−, 0), thereby permitting a check on the reversibility of electrode processes. In addition, dianionic complexes containing bridges with nitrogen donors were found to be labile, as was the case with monoadducts,[8] and attempts to prepare the corresponding neutral complexes yielded only intractable solids.

Polarographic data obtained in dichloromethane solution are summarized in Table II. As in other work[7,8] this solvent was selected to minimize dissociation. Half-wave potentials and diffusion currents were measured in solutions prepared from the preformed complexes or from stoichiometric mixtures of the parent dithiolene dimer and the bridging ligand. Identical polarograms were obtained in the cases in which both

TABLE II

POLAROGRAPHIC DATA FOR BRIDGED BINUCLEAR AND MONONUCLEAR DITHIOLENE COMPLEXES IN DICHLOROMETHANE AT 25°

	$(z = 2-) \rightleftharpoons (z = 1-)$		$(z = 1-) \rightleftharpoons (z = 0)$	
Complex[a]	$E_{1/2}$, V	i_d/C,[b] μA/mM	$E_{1/2}$, V	i_d C,[b] μA/mM
$(tfd)_2Co\text{–}DPPA\text{–}Co(tfd)_2$	+0.46	+40	+0.61	+41
$(tfd)_2Co\text{–}DPPA\text{–}Co(tfd)_2^{2-}$	+0.47	−51	+0.62	−51
$(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2$	+0.43	+48	+0.58	+56
$(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2^{2-}$	+0.43	−49	+0.58	−51
$(tfd)_2Co\text{–}DPPB\text{–}Co(tfd)_2$	~+0.47[c]	+45	~+0.51[c]	+45
$[Co(tfd)_2]_2$	+0.55	+42[d]	+1.23	+50[d]
$(tfd)_2Fe\text{–}DPPE\text{–}Fe(tfd)_2$	+0.31	+57	+0.47[i]	+49
$(tfd)_2Fe\text{–}DPPE\text{–}Fe(tfd)_2^{2-}$	+0.34	−45	+0.69[i]	−38
$[Fe(tfd)_2]_2$	+0.67[e]	. . .	+1.24[e]	. . .
$Co(tfd)_2(DPPA)$[g,j]	*h*	. . .	+0.49	+56
$Co(tfd)_2(DPPE)$[g,j]	*h*	. . .	+0.45	+54
$Co(tfd)_2(DPPB)$[g]	*h*	. . .	+0.47	+47
$Co(tfd)_2(P(C_6H_5)_3)$	. . .	. . .	+0.41[f]	. . .
$Fe(tfd)_2(DPPE)$[g,j]	*h*	. . .	+0.34	+40
$Fe(tfd)_2(DPPB)$[g,j]	*h*	. . .	+0.36	+50
$Fe(tfd)_2(P(C_6H_5)_3)$	. . .	. . .	+0.30[f]	. . .

[a] Initial species is the bridged complex or 1:1 mole ratio of dithiolene dimer and L-L unless otherwise noted. [b] Concentrations calculated on the basis of formulas in first column. [c] Estimated values; waves barely resolvable. [d] Calibration values for one-electron processes; additional values from oxidation of $Cr(mnt)_3^{3-}$ at the same electrode: −44 μA/mM (+0.29 V), −49 μA/mM (+0.82 V). [e] Reference 3. [f] Reference 7. [g] Data obtained in solutions containing either a 2–3-fold or large excess (not accurately measured) of L-L to $[M(tfd)_2]_2^z$. [h] Process not detected. [i] Irreversible. [j] Half-wave potentials and absolute values of diffusion currents are the average of values obtained for z = 2−, 0.

methods were used. Included for comparison purposes are potentials for dithiolene dimers and triphenylphosphine monoadducts. With reference to the binuclear cobalt complexes, which were studied in the most detail, the data reveal two important results. First, two closely spaced waves of approximately or nearly equal diffusion currents are observed in the +0.4–0.6-V range,[32] while the wave at +1.2 V characteristic of the free dithiolene dimer was absent ((L-L) = DPPA) or gave a diffusion current less than ~5% (DPPE) and ~15% (DPPB) of that of the two waves at less positive potentials. Second, polarography of dianionic and neutral species yielded the same half-wave potentials to within 10 mV and nearly equal diffusion currents, which by calibration were found to be consistent with one-electron processes. These results demonstrate the reversibility of these processes, which was also confirmed by cyclic voltammetry. The electrochemical and preparative results permit the formulation of a three-membered electron-transfer series (9) for the binuclear cobalt dithiolenes.

$$(S_4M)\text{–}(L\text{-}L)\text{–}(MS_4)^{2-} \rightleftharpoons (S_4M)\text{–}(L\text{-}L)\text{–}(MS_4)^{-} \rightleftharpoons (S_4M)\text{–}(L\text{-}L)\text{–}(MS_4) \quad (9)$$

Attempts to establish the existence of further reduced members by cathodic polarography of the dianionic or neutral complexes led to the detection of an ill-defined irreversible wave at *ca.* −0.1 V which was not investigated in detail. A wave at +1.53 V (i_d/C = 135 μA/mM) for $(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2^{2-}$ may correspond to a (z = 0) ⇌ (z = 1+ or 2+) process analogous to the (z = 0) ⇌ (z = 1+) oxidation (series (3)) which has been reported for $Co(tfd)_2$ monoadducts.[7] The diffusion current is larger than expected for a two-electron process and waves in this potential region were not investigated further. Iron–tfd complexes with DPPE exhibited two redox steps, but that at the more positive potential is irreversible. Analogous DPPB complexes were too extensively dissociated in solution to warrant detailed polarographic study.

In order to provide further substantiation of the behavior summarized by the series (9) and to search for mononuclear adducts, polarograms were obtained for solutions containing varying $[Co(tfd)_2]_2^z$:(L-L) mole ratios. The results found for (L-L) = DPPA are representative. To a solution containing initially 6.9 × 10^{-4} M dimer successive additions of DPPA produced a decrease in the current of the +1.2-V wave of the former and an increase of current due to a wave with $E_{1/2} \cong$ +0.56 V. At ratios below 1.3 resolvable waves at +0.46 and +0.61 V appeared, and at a ratio of unity the +1.2-V wave was no longer observable. Gradual decrease of the ratio to 0.3 resulted in the appearance of a single wave at +0.48 V and no appreciable change in diffusion current. The wave at +1.2 V remained undetectable. This behavior is attributed to conversion of the binuclear complex to the mononuclear adduct by reaction 10. Because equilibrium constants are unknown, the extent of mononuclear adduct formation is uncertain. However, addition of even larger excesses

$$(S_4M)\text{–}(L\text{-}L)\text{–}(MS_4)^z + L\text{-}L \rightleftharpoons 2(MS_4)(L\text{-}L)^{z/2} \quad (10)$$

of bridging ligand in this and other cases caused no further significant changes in $E_{1/2}$ and i_d values. The potentials quoted in Table II for the (z = 1−) ⇌ (z = 0) process of the mononuclear adducts were obtained by experiments of this type and are possibly in error by *ca.* 10–20 mV since the waves in question may be a superposition of those for mono- and binuclear species in the +0.4–0.6-V range. The same process for $Co(tfd)_2(P(C_6H_5)_3)$ has $E_{1/2}$ = +0.41 V.[7] The free bridging ligands are not electroactive in this range of potentials.

The data in Table II show that the $E_{1/2}$ values for the two redox processes of bridged binuclear cobalt complexes and the single process of the mononuclear adducts occur in a range of only 0.2 V. In terms of oxidation the (z = 2−) ⇌ (z = 1−) process of the binuclear complexes occurs at nearly the same potential as the (z = 1−) ⇌ (z = 0) process of the mononuclear species, 0.43–0.47 and 0.41–0.48 V, respectively, despite the larger negative charge of the former. Further, the second oxidation of the binuclear complexes occurs at potentials only slightly more positive (0.51–0.62 V) than those of the first oxidation. Because the dithiolene units are the redox-active sites in the dimers, the half-wave potentials indicate that these units behave as remote (*i.e.*, essentially independent) sites in the electron-transfer reactions.

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[32] While these waves are observable in conventional dc polarograms, their presence was additionally verified in cyclic and derivative polarograms.

Magnetic Properties.—Magnetic moments of solids at ~25° are listed in Table III. Moments per iron or cobalt are consistent with those determined for mononuclear analogs.[7,8] Thus, moments of $(FeS_4)L^-$ complexes with L = py and PR_3[33] correspond to ground-state spins of $^3/_2$ and $^1/_2$, respectively, while those of $Co(tfd)_2(PR_3)$ correspond to a spin of $^1/_2$. $(FeS_4)(PR_3)$ and $CoS_4(PR_3)^-$ complexes are diamagnetic. Moments of several of the neutral cobalt complexes are slightly less than the spin-only value for $S = {}^1/_2$. In the absence of measurements over a temperature range the significance of these values is unclear. Uncertainties in the large diamagnetic corrections to the measured susceptibilities may be responsible in part for the low values.

TABLE III

MAGNETIC MOMENTS OF SOLID COMPLEXES AT ~25°

Complex[a,b]	μ_{eff}(Fe, Co),[c] BM	Spin(Co, Fe)
$(mnt)_2Fe\text{–}pyz\text{–}Fe(mnt)_2^{2-}$	3.98	$^3/_2$
$(mnt)_2Fe\text{–}4,4'\text{-}bipy\text{–}Fe(mnt)_2^{2-}$	4.11	$^3/_2$
$(mnt)_2Fe\text{–}pySSpy\text{–}Fe(mnt)_2^{2-}$	4.10	$^3/_2$
$(mnt)_2Fe\text{–}pyC_2H_2py\text{–}Fe(mnt)_2^{2-}$	4.15	$^3/_2$
$(mnt)_2Fe\text{–}pyC_2H_4py\text{–}Fe(mnt)_2^{2-}$	4.17	$^3/_2$
$(mnt)_2Fe\text{–}DPPB\text{–}Fe(mnt)_2^{2-}$	1.93	$^1/_2$
$(tfd)_2Fe\text{–}pyz\text{–}Fe(tfd)_2^{2-}$	4.01	$^3/_2$
$(tfd)_2Fe\text{–}4,4'\text{-}bipy\text{–}Fe(tfd)_2^{2-}$	4.08	$^3/_2$
$(tfd)_2Fe\text{–}DPPB\text{–}Fe(tfd)_2^{2-}$	2.31	$^1/_2$
$(tfd)_2Fe\text{–}DPPB\text{–}Fe(tfd)_2$	Dia	0
$(tfd)_2Fe\text{–}DPPE\text{–}Fe(tfd)_2^{2-}$	1.93	$^1/_2$
$(tfd)_2Fe\text{–}DPPE\text{–}Fe(tfd)_2$	Dia	0
$(mnt)_2Co\text{–}DPPB\text{–}Co(mnt)_2^{2-}$	Dia	0
$(tfd)_2Co\text{–}DPPB\text{–}Co(tfd)_2$	1.59	$^1/_2$
$(tfd)_2Co\text{–}DPPB\text{–}Co(tfd)_2^{2-}$	Dia	0
$(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2^{2-}$	Dia	0
$(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2$	1.69	$^1/_2$
$(tfd)_2Co\text{–}DPPA\text{–}Co(tfd)_2^{2-}$	Dia	0
$(tfd)_2Co\text{–}DPPA\text{–}Co(tfd)_2$	1.62	$^1/_2$
$Fe(mnt)_2py^-$, $Fe(tfd)_2py^-$	4.18, 3.98	$^3/_2$
$Fe(tfd)_2P(C_6H_5)_3$	Dia[7]	0
$Co(tfd)_2P(C_6H_5)_3^z$, $z = 0, 1-$	1.75, dia[7]	$^1/_2$, 0

[a] Anions measured as $(n\text{-}C_4H_9)_4N^+$ salts. [b] All compounds listed in Table I but not included here are diamagnetic. [c] Diamagnetic corrections calculated from Pascal's constants or obtained from the measured susceptibility of an analogous diamagnetic cobalt or iron complex.

The neutral binuclear cobalt complexes were examined by epr since their magnetic moments suggested the existence of independent or very weakly coupled dithiolene units with $S = {}^1/_2$. With DPPA no epr signal was observable at 25°. The DPPB complex gave a broad signal with no resolved hyperfine splitting. A poorly resolved eight-line spectrum (^{59}Co, $I = {}^7/_2$) was observed for the DPPE complex. Addition of excess bridging ligand in each case yielded an eight-line spectrum nearly superimposable on the spectrum of $Co(tfd)_2(P(C_6H_5)_3)$.[7] Values of $\langle g \rangle$ in dichloromethane solution for $Co(tfd)_2(P(C_6H_5)_3)$ and $Co(tfd)_2(L\text{-}L)$ ((L-L) = DPPB, DPPE, and DPPA) are, respectively, 2.021 (lit.[7] 2.0192), 2.021, 2.024, and 2.028. These spectra are attributed to mononuclear adducts, which were detected polarographically under similar concentration and temperature conditions. Dichloromethane solutions containing equimolar amounts of neutral and dianionic DPPA complexes yielded an apparent eight-line spectrum exhibiting different resolution from that of the mononuclear adduct with $\langle g \rangle = 2.028$ and variable hyperfine splittings of *ca.* 27–33 G. This spectrum may be due to $(tfd)_2Co\text{–}DPPA\text{–}Co(tfd)_2^-$, but because of poor resolution and the variable splittings, further interpretation was not warranted. Apparent hyperfine splittings of all of the above species are also variable, an effect which may be due to unresolved interaction with other magnetic nuclei and relaxation effects. Attempts to isolate monoanionic species from reactions of neutral and dianionic complexes in dichloromethane were unsuccessful.

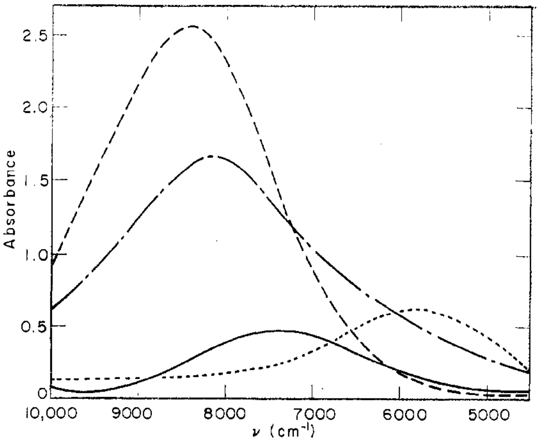

Figure 2.—Electronic spectra of $(tfd)_2Co\text{–}DPPE\text{–}Co(tfd)_2^z$ in dichloromethane: ---, $z = 2-$; · · · ·, $z = 0$; -·-·-, equimolar mixture of $z = 2-, 0$; ——, difference spectrum. Spectra refer to 5×10^{-4} *M* solutions and were measured in 2-cm cells.

Electronic Spectra.—Polarographic half-wave potentials indicate that a 1:1 mixture of neutral and dianionic Co–tfd dimers with DPPA or DPPE bridges should yield predominantly $(tfd)_2Co\text{–}(L\text{-}L)\text{–}Co(tfd)_2^-$. The analogous species with DPPB should be considerably more unstable to disproportionation due to the small difference between its $E_{1/2}$ values. Because the polarographic data also suggest that in the monoanion charge is localized on one of the two cobalt dithiolene units, it was of interest to search for the electronic absorption corresponding to the electron transfer between these two units. Examination of the spectra of dichloromethane solutions containing initially equimolar amounts of $z = 2-$ and 0 complexes revealed that the largest difference from additivity of the spectral absorbances of the separately measured complexes occurred in the near-infrared region. Relevant spectra for the DPPE system are shown in Figure 2. The

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(33) The complex with a magnetic moment of 3.97 BM which was originally formulated[7] as $Fe(tfd)_2(P(C_6H_5)_3)^-$ has since been shown to be $Fe(tfd)_2(OP(C_6H_5)_3)^-$.[9] The low-spin moments of the two dianionic iron–DPPB species imply that the as yet unisolated $Fe(tfd)_2(P(C_6H_5)_3)^-$ should also have a moment consistent with $S = {}^1/_2$. To check on the presence of phosphine oxide in the binuclear iron complexes, a sample of $((n\text{-}C_4H_9)_4N)_2[(tfd)_2Fe\text{–}DPPB\text{–}Fe(tfd)_2]$ (2.31 BM) dissolved in a dichloromethane–toluene mixture was chromatographed on alumina. The colorless toluene eluate was evaporated to dryness and the residue was recrystallized from toluene–heptane to afford a 70% recovery of DPPB, identified by its melting point and infrared spectrum. The monoxide and dioxide of DPPB[23] were not detected.

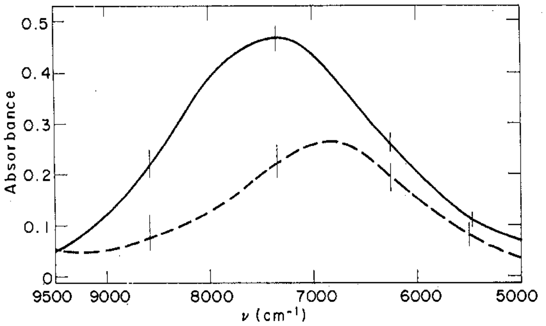

Figure 3.—Intervalence electron-transfer absorption bands of $(tfd)_2Co-(L\text{-}L)-Co(tfd)_2^-$ in dichloromethane: ———, (L-L) = DPPE; ----, (L-L) = DPPA. Spectra refer to 5×10^{-4} *M* solutions initially equimolar in $z = 2-$ and 0 complexes in 2-cm cells and were obtained by difference. The vertical lines indicate the approximate uncertainty in absorbance.

difference spectrum consists of a well-defined band at ~7350 cm^{-1} which is within the energy range expected for intervalence electron-transfer absorptions.[16,34–36] At higher energies the difference spectrum contained weaker bands ($\lesssim 20\%$ deviation from additivity), which are attributed to concentration-dependent dissociation and shifts in band maxima for the $z = 1-$ complex relative for the $z = 2-$, 0 species. The above spectral interpretations are provisional, since the spectral bands of the $z = 2-$, 0 species have not been assigned. Similar results were obtained for the DPPA system, but no analogous absorption band could be detected in the DPPB system. The two electron-transfer bands are shown in Figure 3. Additional spectral studies showed that these bands are not due to mononuclear adducts or $[Co(tfd)_2]_2$. Following previously published arguments,[34b,36] the energies (E_{op}) of these bands may be used to estimate the intramolecular electron-transfer rate constants: $(tfd)_2Co-DPPA-Co(tfd)_2^-$, $E_{op} = 6850$ cm^{-1}, $k = 2 \times 10^9$ sec^{-1}; $(tfd)_2Co-DPPE-Co(tfd)_2^-$, $E_{op} = 7350$ cm^{-1}, $k = 9 \times 10^8$ sec^{-1}. These values are consistent with the expectation that interaction between the two metal centers would be larger with the shorter DPPA bridge and are similar in magnitude to other cases[16,36] where two metal centers in the same ion are separated by *ca.* 4–7 Å. However, any attempt to account quantitatively for differences in the preceding quantities must await preparation of a more extensive series of complexes exhibiting intervalence electron-transfer processes.

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[34] (a) G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, **8**, 357 (1967); (b) N. S. Hush, *ibid.*, **8**, 391 (1967).

[35] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

[36] D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, **92**, 219 (1970).

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Mixed-Ligand Complexes of Cobalt(III). *trans*-Bis(amino acid)(tetramine)cobalt(III) Complexes

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The syntheses and some properties of cobalt(III) complexes with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine and alanine are reported. Comparison of the properties of these complexes with those of the corresponding acetate derivatives indicates that the amino acid residues are bonded to mutually trans sites through the carboxyl groups.

Introduction

Complexes of cobalt(III) with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) show a marked preference for the trans topology.[1–3] In contrast, complexes with triethylenetetramine (trien or 2,2,2-tet) most commonly adopt a cis geometry.[4,5] Similarly, the sulfur-containing ligands 3,7-dithia-1,9-nonanediamine (ete) and 4,7-dithia-1,10-decanediamine (tet) readily adopt the trans geometry[6] which is not found for complexes with 3,6-dithia-1,8-octanediamine (eee).[7] As a part of our continuing study of the steric course of some reactions of mixed-ligand cobalt(III) complexes, we have utilized the demonstrated preference of long-chain flexible tetradentate ligands for the trans topology in the synthesis of some novel *trans*-bis(amino acid)-(tetramine)cobalt(III) complexes.

Experimental Section

Physical Measurements. Electronic and Circular Dichroism

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[1] H. G. Hamilton and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

[2] H. G. Hamilton and M. D. Alexander, *J. Amer. Chem. Soc.*, **89**, 5065 (1967).

[3] H. G. Hamilton and M. D. Alexander, *Inorg. Chem.*, **8**, 2131 (1969).

[4] A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).

[5] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

[6] B. Bosnich, W. R. Kneen, and A. T. Phillip, *ibid.*, **8**, 2567 (1969).

[7] J. H. Worrell and D. H. Busch, *ibid.*, **8**, 1563, 1572 (1969).