exchange on $[Cr(dmf)_6]^{3+}$ $(\Delta V^* = -6.3 \text{ cm}^3 \text{ mol}^{-1})$[15] and $[Ni(dmf)_6]^{2+}$ $(\Delta V^* = +9.1 \text{ cm}^3 \text{ mol}^{-1})$.[16] As these two species are of similar size to $[Cu(Me_6tren)dmf]^{2+}$ $(\Delta V^* = +6.1 \pm 0.1$ $\text{cm}^3 \text{ mol}^{-1})$, characterizing this species is interpreted in terms of a d activation mode. Although it appears to be possible to discriminate between dissociative (D) and dissociative interchange (i_d) mechanisms from the magnitude of ΔV^* for water exchange, such does not appear to be the case for the more complicated dmf molecule.[13] Nevertheless, as ΔV^* observed for $[Ni(dmf)_6]^{2+}$ is larger than that for $[Cu(Me_6tren)dmf]^{2+}$, it is probable that the latter species is characterized by an I_d mechanism for dmf exchange. The negative ΔS^* value is at first sight unexpected for a d activated mechanism, but if solvent rearrangements outside the first coordination sphere and vibrational and rotational changes within the first coordination sphere together or separately make significant contributions to this parameter, then its sign becomes of dubious value in mechanistic interpretations.[17,18]

The general similarity of k_i characterizing anation by NCS^-, N_3^-, and Br^- to k_{ex} (Table I) suggests that dissociation of dmf from $[Cu(Me_6tren)dmf]^{2+}$ is the major rate-determining factor in the anation reaction. In view of this and the variation of k_{obsd} according to eq 6 it is probable that an I_d mechanism

characterizes the anation of $[Cu(Me_6tren)dmf]^{2+}$. (A D mechanism would also be characterized by a rate law of similar form to eq 6, but as the opposite charges of $[Cu(Me_6tren)-dmf]^{2+}$ and X^- render the formation of encounter complexes inevitable under the conditions of this study, experimental distinction between the D and I_d mechanisms is virtually impossible.) By contrast the anation of $[Cr(dmf)_6]^{3+}$ by X^-, which appears to be a classic example of the operation of an associative interchange (I_a) mechanism, is characterized by $k_i/k_{ex} = 0.088$, 1.03, 2.35, and 57.5 at 344.5 K when $X^- = Br^-$, Cl^-, NCS^-, and N_3^-, respectively.[19]

(15) Lo, S. T. D.; Swaddle, T. W. *Inorg. Chem.* **1975**, *14*, 1878.
(16) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2142.
(17) Caldin, E. F.; Bennetto, H. P. *J. Solution Chem.* **1973**, *2*, 217.
(18) Fischer, P.; Hoffman, H.; Platz, G. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 1060.

(19) Lo, S. T. D.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 1881. (In the inert $[Cr(dmf)_6]^{3+}$ system where the slow formation of $[Cr(dmf)_5X]^{2+}$ permits the direct determination of dmf exchange in the encounter complex, it has been shown that X^- (Cl^-, Br^-, N_3^-, or NCS^-) at most reduces the rate of dmf exchange on $[Cr(dmf)_6]^{3+}$ to the small extent expected statistically as a consequence of the displacement of one dmf from the second coordination sphere. It is reasonable to assume that a similar situation prevails in the $[Cu(Me_6tren)dmf]^{2+}$ system, but a direct examination of this aspect is not possible due to the lability of the system.)

Contribution from the Department of Chemistry,
Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Solvation and Ionic Association of Bis(2,4-pentanedionato)(diamine)cobalt(III) Complexes in Nitrobenzene and 1,2-Dichloroethane

KAZUAKI ITO

The conductances of 11 bis(2,4-pentanedionato)(diamine)cobalt(III) complexes ($[Co(acac)_2(diamine)]X$ where diamine = en (ethylenediamine), pn (1,2-propanediamine), N,N-dmen (N,N-dimethylethylenediamine), N,N'-dmen (N,N'-dimethylethylenediamine), N,N,N'-trimen (N,N,N'-trimethylethylenediamine), N,N,N',N'-tmen (N,N,N',N'-tetramethylethylenediamine), 2-ampy (2-(aminomethyl)pyridine), and bpy (2,2'-bipyridine) and where $X^- = ClO_4^-$ and I^-) were measured in nitrobenzene (PhNO$_2$) and 1,2-dichloroethane (1,2-DCE) at 25 °C. It was found that the mobilities of $[Co(acac)_2(diamine)]^+$ in PhNO$_2$ increase with the introduction of the N-methyl groups, whereas those in 1,2-DCE are approximately constant. The mobility of $[Co(acac)_2(bpy)]^+$ in PhNO$_2$ is more retarded than that in 1,2-DCE. The association constants decrease with the decrease in the number of the NH protons in both solvents except for $[Co(acac)_2(N,N'$-dmen)]ClO$_4$ in PhNO$_2$. These results were explained in terms of the specific ion–solvent interactions: (a) the change in hydrogen-bonding activity of the NH protons in the chelate cations due to both the solvation and the desolvation accompanying the introduction of the substituents and (b) the π–π interaction between nitrobenzene and $[Co(acac)_2(bpy)]^+$.

Introduction

Metal chelate electrolytes, in which a metal cation is surrounded by aromatic and aliphatic ligands, have recently been noted as unique electrolytes. The characteristics of their solute–solvent interactions, concerning charge, size, and chemical properties of ligands, have been elucidated by the studies of salting in,[1] ion-pair extraction,[2] electronic spectra,[3] racemization,[4] optical resolution,[5] viscosity and molal volume,[6] and

conductivity.[7-13] Among these, the conductivity measurements are useful as an effective means to understand the nature of

(1) (a) Iwamoto, E.; Hiyama, Y.; Yamamoto, Y. *J. Solution Chem.* **1977**, *6*, 371. (b) Iwamoto, E.; Tanaka, Y.; Kimura, H.; Yamamoto, Y. *Ibid.* **1980**, *9*, 841.
(2) Yamamoto, Y.; Tarui, T.; Iwamoto, E.; Tarumoto, T. *Anal. Chim. Acta* **1976**, *84*, 217.
(3) (a) Fukuda, Y.; Sone, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 465. (b) Fukuda, Y.; Sone, K. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2315.

(4) (a) Iwamoto, E.; Fujiwara, T.; Yamamoto, Y. *Inorg. Chim. Acta* **1980**, *43*, 95. (b) Van Meter, F. M.; Newmann, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 1382, 1388.
(5) (a) Iwamoto, E.; Yamamoto, M.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 399. (b) Yamamoto, M.; Iwamoto, E.; Kozasa, A.; Takemoto, K.; Yamamoto, Y.; Tatehata, A. *Ibid.* **1980**, *16*, 77.
(6) (a) Tominaga, T.; *J. Phys., Chem.* **1975**, *79*, 1664. (b) Yamamoto, Y.; Tominaga, T.; Tagashira, S. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 825.
(7) Millen, W. A.; Watts, D. W. *J. Am. Chem. Soc.* **1967**, *89*, 6858.
(8) Pethybridge, A. D.; Spiers, D. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 64, 73.
(9) (a) Yamamoto, Y.; Sumimura, E.; Miyoshi, K.; Tominaga, T. *Anal. Chim. Acta* **1973**, *64*, 226. (b) Miyoshi, K. *J. Phys. Chem.* **1972**, *76*, 3029. (c) Miyoshi, K.; Tominaga, T. *Ibid.* **1973**, *77*, 519, 819.
(10) Newmann, D. S.; Blinn, E.; Carison, B. L. *J. Phys. Chem.* **1979**, *83*, 676.

solute–solvent interactions since the degree of ion pairing and the ionic mobility is exceedingly sensitive to the interactions.[14,15]

The conductance studies in dimethyl sulfoxide and water of *cis*- and *trans*-[CoXY(en)₂]⁺ complexes,[7,8] where X and Y represent one of the ligands Cl, Br, and NO₂, indicated that both the dipolar nature of the cis complexes and the hydrogen-bonding donor properties of the NH protons of ethylenediamine are important in their ionic association process; the association constant of the cis complexes is larger and their mobility is smaller than those of trans complexes. The Cl⁻ ion was more associated with [M(en)₃]³⁺ (M = Co, Cr) in water than with [M(NH₃)₆]³⁺ while the reverse was found for the SO₄²⁻ and C₂O₄²⁻ ions,[11,12] suggesting the importance of the hydration of the NH protons. However, most studies reported to date were concerned with water and organic solvents of high dielectric constant because of the limitation of complex solubilities. The conductances in low dielectric media were reported only for [Cu(dmp)₂]ClO₄ (dmp = 2,9-dimethyl-1,10-phenanthroline),[9b,c] in which the cation is surrounded by bulky aromatic groups.

The metal chelate electrolytes [Co(acac)₂(diamine)]X are soluble even in low-dielectric solvents such as 1,2-dichloroethane (dielectric constant $D = 10.36$) and were confirmed to be stable by both spectrophotometry and conductometry. Low-dielectric 1,2-DCE has been used as a medium for ligand-exchange reactions and racemization of bulky aromatic 1,10-phenanthroline complexes.[16] Since the properties of the [Co(acac)₂(diamine)]⁺ cations are changeable stepwise by the replacement of the substituents such as NH protons, these cations are suited for clarifying the various aspects of solvation of octahedral complexes. Alkylammonium and pyridinium ions with NH protons have so far been used as molecular probes.[17,18] The conductance of the electrolytes in various solvents is increased with the addition of basic molecules such as alkylamine and pyridine due to hydrogen-bond formation, reflecting the short-range ion–solvent interaction between ions and basic molecules and the effect of bulk solvents.

We have clarified that the association constant of [Co-(acac)₂(*N,N′*-dmen)]Br in nitrobenzene is large compared with that of [Co(acac)₂(en)]Br.[13] The purpose of the present study is to elucidate the influence of the introduction of methyl and pyridine groups into the diamine of [Co(acac)₂(diamine)]⁺ complexes on ionic association and mobility in nitrobenzene and 1,2-dichloroethane. These solvents are both aprotic and weak in donicity, but they have different dielectric constants and solvent properties due to aromatic and aliphatic groups. The iodide and perchlorate salts were employed because of their ease of dissolution. Thus, it is considered that there are two factors governing the conductance behavior of the electrolytes in these solvents: One is the polarity of solvent molecules, and the other, the π–π interactions between nitrobenzene molecules and the aromatic ligands in the chelate cations.

Experimental Section

Materials. 2,4-Pentanedione and diamine (en, pn, *N,N*-dmen, *N,N′*-dmen, *N,N,N′*-trimen, *N,N,N′,N′*-tmen, 2-ampy, and bpy) were of reagent grade and were used without further purification. Na-[Co(acac)₂(NO₂)₂], which is a starting material for the preparation of [Co(acac)₂(diamine)]X, was prepared from Na₃[Co(NO₂)₆] and purified according to the method of Bailor et al.[19] [Co(acac)₂(diamine)]X (X⁻ = ClO₄⁻, I⁻) was prepared by mixing Na[Co-(acac)₂(NO₂)₂] with equimolar solutions of the corresponding diamine in cold water–methanol mixtures and addition of aqueous solution of 6 M NaX. The iodide and perchlorate salts were purified by the same method as for [Co(acac)₂(en)]ClO₄ and [Co(acac)₂(bpy)]I, respectively.[20] The tetraalkylammonium salts, Bu₄NClO₄ and Et₄NClO₄, were commercial products.

All the samples were purified by at least three recrystallizations and dried in vacuo at 50 °C and stored in brown glass bottles in desiccators over phosphorus pentoxide. The purity of the salts was checked by analysis. The *N,N′*-dmen complex can be distinguished from the *N,N*-dmen complex by infrared and NMR measurements. The N–H stretching bands are at 3228 cm⁻¹ for the *N,N′*-dmen complex and 3252 and 3310 cm⁻¹ for the *N,N*-dmen complex. The δ values from internal Me₄Si are 4.70 and 5.30 with equal intensity for the *N,N′*-dmen complex and 4.57 for the *N,N*-dmen complex in nitrobenzene. For the iodide salts the purity was checked by potentiometric titration with siver nitrate.

Nitrobenzene (PhNO₂) was purified as described previously.[13] 1,2-Dichloroethane (1,2-DCE) was washed with sodium hydrogen carbonate solution and then with water, dried over anhydrous calcium chloride for 1 week, and fractionally distilled. The middle fraction was collected. Density (d in g cm⁻³), viscosity (η in mPa s), and specific conductance of pure solvent (κ in S cm⁻¹) at 25 °C: PhNO₂ d = 1.1983, η = 1.847, $\kappa \approx 4 \times 10^{-10}$; 1,2-DCE d = 1.2456, η = 0.7846, $\kappa \approx 4 \times 10^{-10}$.

Apparatus and Measurements. Conductances were measured at 1592 Hz by an LCR type instrument (Ando Electric Co. Ltd.), which was calibrated with a standard resistance box (Shimazu Seisakusho Co.). The conductivity cells were of the Kraus–Erlenmeyer type with lightly platinized electrodes. In the case of [Co(acac)₂(bpy)]⁺ however, the electrode was not platinized because this complex was decomposed, as was seen in some other Co(III) complexes.[8] The cell constants were determined by the semiempirical equation of Lind, Zwolenik, and Fuoss[21] for the molar conductivity of KCl solutions (0.001–0.01 mol L⁻¹) at 25 °C. KCl was recrystallized twice from conductivity water and dried at 500 °C. All measurements were carried out in a water bath thermostated to 25 ± 0.005 °C, the solutions in the cell being stirred by a magnetic stirrer. For [Co(acac)₂(en)]I and [Co-(acac)₂(pn)]I in 1,2-DCE, a slight increase in resistance with time was observed. Therefore, a small correction was made by extrapolating to time zero. Stock solutions were prepared by weight and corrected to vacuum, and the concentration was calculated by using the density. Measurements were carried out by a dilution technique to an appropriate concentration. A linear relationship between density and molarity was assumed in all cases for our solutions, which are sufficiently dilute for this to be reasonable. The preparation of the solutions was made in a drybox.

Density and viscosity were measured with a digital density meter (Anton Paar Model DMA 02D) and Ubbelohde viscometer modified for use in a closed, dry atmosphere at 25 ± 0.01 °C, respectively. Visible spectra were obtained with a Hitachi Model 210-10 spectrometer.

Results

The measured equivalent conductances Λ (S cm² mol⁻¹) and the corresponding electrolyte concentrations C (mol L⁻¹) are given as supplementary material for nitrobenzene and 1,2-

(11) Jenkins, I. L.; Monk, C. B. *J. Chem. Soc.* **1951**, 68.
(12) (a) Tanaka, N.; Kobayashi, Y.; Kamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2939. (b) Tanaka, N.; Yamada, A. *Fresenius' Z. Anal. Chem.* **1967**, *224*, 117. (c) Takahashi, T.; Koiso, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2784. (d) Takahashi, T.; Koiso, T. *Ibid.* **1978**, *51*, 1307.
(13) Ito, K.; Iwamoto, E.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3190.
(14) Kay, R. L.; Evans, D. F.; Matesich, M. A. "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D. Eds.; Marcel Dekker: New York, 1976; Vol. 2, Chapter 10.
(15) Fernández-Prini, R.; Spiro, M. "Physical Chemistry of Organic Solvent Systems"; Covington, A. K., Dickinson, T., Eds.; Plenum Press: New York, 1973; Chapter 5.
(16) (a) Fujiwara, T.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 635. (b) Fujiwara, T.; Matsuda, K.; Yamamoto, Y. *Ibid.* **1980**, *16*, 301.
(17) (a) Ralph, E. K., III; Gilkerson, W. R. *J. Am. Chem. Soc.* **1964**, *86*, 4783. (b) Gilkerson, W. R.; Ezell, J. B. *Ibid.* **1967**, *89*, 808. (c) Junker, M. L.; Gilkerson, W. R. *Ibid.* **1975**, *97*, 493. (d) Jackson, M. D.; Gilkerson, W. R. *Ibid.* **1979**, *101*, 328. (e) Gilkerson, W. R.; Jackson, M. D. *Ibid.* **1979**, *101*, 4096.
(18) (a) Pirson, D. J.; Huyskens, P. L. *J. Solution Chem.* **1974**, *3*, 503. (b) Haulait, M. C.; Huyskens, P. L. *J. Phys. Chem.* **1975**, *79*, 1812. (c) Van Evan, V.; Haulait-Pirson, M. C. *J. Solution Chem.* **1977**, *6*, 757. (d) Haulait-Pirson, M. C.; De Pauw, M. *J. Phys. Chem.* **1980**, *84*, 1381. (e) Pawelka, Z.; Haulait-Pirson, M. C. *Ibid.* **1981**, *85*, 1052.

(19) Bucher, L. J.; Bailor, J. C., Jr. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1093.
(20) Arcker, R. D.; Cotsoradis, B. P. *Inorg. Chem.* **1965**, *4*, 1584.
(21) Lind, J. E.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1559.

Table I. Derived Parameters in Nitrobenzene at 25 °C

electrolyte	Λ_0, S cm^2 mol^{-1}	K_a, L mol^{-1}	d, Å	σ_Λ, S cm^2 mol^{-1}
[Co(acac)$_2$(en)]ClO$_4$	31.770 ± 0.007	56 ± 1	12.0	0.004
[Co(acac)$_2$(pn)]ClO$_4$	31.42 ± 0.02	56 ± 3	12.2	0.014
[Co(acac)$_2$(N,N-dmen)]ClO$_4$	32.380 ± 0.004	44 ± 1	11.5	0.003
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	31.90 ± 0.02	59 ± 2	11.7	0.016
[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$	32.429 ± 0.008	40 ± 5	9.9	0.006
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$	32.82 ± 0.01	23 ± 2	11.7	0.007
[Co(acac)$_2$(2-ampy)]ClO$_4$	31.118 ± 0.006	49 ± 1	12.8	0.003
[Co(acac)$_2$(bpy)]ClO$_4$	30.841 ± 0.006	33 ± 1	13.4	0.005
[Co(acac)$_2$(en)]I	31.70 ± 0.02	149 ± 1	18.0	0.020
[Co(acac)$_2$(pn)]I	31.40 ± 0.02	122 ± 2	15.2	0.017
[Co(acac)$_2$(bpy)]I	30.92 ± 0.02	39 ± 2	15.5	0.008
Bu$_4$NClO$_4$	32.718 ± 0.008	40 ± 1	11.3	0.006
Bu$_4$NI^a	32.780 ± 0.006	58 ± 1	19.5	0.002
Et$_4$NClO$_4$	37.32 ± 0.01	36 ± 2	9.7	0.008

^{a} From ref 25a.

Table II. Derived Parameters in 1,2-Dichloroethane at 25 °C

electrolyte	Λ_0, S cm^2 mol^{-1}	K_a, L mol^{-1}	d, Å	σ_Λ, S cm^2 mol^{-1}
[Co(acac)$_2$(en)]ClO$_4$	64.85 ± 0.40	16600 ± 600	20.2	0.13
[Co(acac)$_2$(pn)]ClO$_4$	63.62 ± 0.33	13700 ± 400	19.0	0.09
[Co(acac)$_2$(N,N-dmen)]ClO$_4$	65.18 ± 0.21	9740 ± 440	20.5	0.16
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	64.33 ± 0.40	11100 ± 900	20.4	0.22
[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$	64.58 ± 0.40	5910 ± 820	18.7	0.36
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$	65.22 ± 0.04	2100 ± 50	24.5	0.04
[Co(acac)$_2$(2-ampy)]ClO$_4$	62.60 ± 0.18	11600 ± 400	20.4	0.12
[Co(acac)$_2$(bpy)]ClO$_4$	62.38 ± 0.07	2520 ± 140	22.3	0.03
[Co(acac)$_2$(en)]I	62.14 ± 0.11	39500 ± 300	22.2	0.04
[Co(acac)$_2$(pn)]I	59.95 ± 0.26	25800 ± 700	36.5	0.05
[Co(acac)$_2$(bpy)]I	58.60 ± 0.15	3040 ± 790	26.3	0.06
Bu$_4$NClO$_4$^{a}	65.16 ± 0.04	6320 ± 60	20.1	0.03

^{a} From ref 25c.

dichloroethane solutions of [Co(acac)$_2$(diamine)]X and R$_4$NClO$_4$.

The data were analyzed by the Fuoss–Hsia equation[22a] with Ferñandez-Prini coefficients[22b] and a hydrodynamic effect discovered by Chen[22c] ($E = E_1\Lambda_0 - 2E_2$):

$$\Lambda = \gamma(\Lambda_0 - SC^{1/2}\gamma^{1/2} + EC\gamma \log (C\gamma) + J_1(d)\ C\gamma + J_2(d)\ C^{3/2}\gamma^{3/2}) \quad (1)$$

$$K_a = (1 - \gamma)/\gamma^2 Cf_\pm^2 \quad (2)$$

The mean ionic activity coefficient $f_\pm$ is given by the extended Debye–Hückel equation

$$-\log f_\pm = A(C\gamma)^{1/2}/[1 + BR(C\gamma)^{1/2}] \quad (3)$$

In the above equations the symbols have their usual meaning.

The procedure of fitting is first to adjust Λ_0 and K_a corresponding to each d from 0.05 to 25 for PhNO$_2$ and from 3 to 40 for 1,2-DCE at 1-Å intervals and then to choose the best-fit values of Λ_0, K_a, and d corresponding to the minimum standard deviation σ_Λ calculated by means of the expression

$$\sigma_\Lambda = [\sum(\Lambda_{obsd} - \Lambda_{calcd})^2/(N - 3)]^{1/2} \quad (4)$$

where N is the number of experimental points.

The appearance of two minima of σ_Λ on the d values was obtained for almost all PhNO$_2$ systems although one minimum for 1,2-DCE was predominant. The appearance of two minima was frequently observed, and the correlations of d values with critical distances q ($=e^2/2DkT$) were discussed,[23] where e is the electric charge, D the dielectric constant, k the Boltzmann constant, and T the absolute temperature. Justice et al.[24]

Table III. Ionic Mobilities and Walden Products in Nitrobenzene and 1,2-Dichloroethane

	λ_0^+ ($\lambda_0^+\eta$)	
	nitrobenzene	1,2-dichloroethane
[Co(acac)$_2$(en)]$^+$	10.9 (0.201)	25.7 (0.201)
[Co(acac)$_2$(pn)]$^+$	10.5 (0.194)	24.4 (0.192)
[Co(acac)$_2$(N,N-dmen)]$^+$	11.5 (0.212)	26.0 (0.204)
[Co(acac)$_2$(N,N'-dmen)]$^+$	11.0 (0.203)	25.1 (0.197)
[Co(acac)$_2$(N,N,N'-trimen)]$^+$	11.5 (0.213)	25.4 (0.199)
[Co(acac)$_2$(N,N,N',N'-tmen)]$^+$	11.9 (0.220)	26.0 (0.204)
[Co(acac)$_2$(2-ampy)]$^+$	10.2 (0.189)	23.4 (0.184)
[Co(acac)$_2$(bpy)]$^+$	9.9 (0.184)	23.2 (0.182)
Bu$_4$N$^+$	11.8 (0.218)	26.0 (0.204)

employed the critical distance as a distance parameter d in J terms. In this study, if two minima were observed, the one at the d closer to the critical distance was adopted ($q = 8.05$ Å for PhNO$_2$ and 28.4 Å for 1,2-DCE). The conductance parameters obtained are given in Tables I and II for PhNO$_2$ and 1,2-DCE, respectively.

Some indication for the precision of the data (Tables I and II) can be obtained from the values of Λ_0 ([Co(acac)$_2$(diamine)]I) – Λ_0([Co(acac)$_2$(diamine)]ClO$_4$) (diamine = en, pn, bpy) in PhNO$_2$ and 1,2-DCE and Λ_0([Co(acac)$_2$(diamine)]Br)[13] – Λ_0([Co(acac)$_2$(diamine)]ClO$_4$) (diamine = en, N,N-dmen, N,N'-dmen, N,N,N',N'-tmen) in PhNO$_2$. The iodide–perchlorate difference is found to be negligible, and the bromide–perchlorate difference is 0.40 ± 0.05 in nitrobenzene. These results are furthermore compared to the values, 0.1 and 0.6 of the Λ_0(Bu$_4$NI)[25a] – Λ_0(Bu$_4$NClO$_4$) and Λ_0(Bu$_4$NBr)[25b] – Λ_0(Bu$_4$NClO$_4$) differences, respectively. The iodide–perchlorate difference in 1,2-dichloroethane is 3.4 ± 0.5.

(22) Fuoss, R. M.; Hsia, K. L. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 1550. (b) Ferñández-Prini, R. *Trans. Faraday Soc.* **1969**, *65*, 3311. (c) Chen, M. S. Ph.D. Dissertation, Yale University, 1969.

(23) (a) Hanna, E. M.; Pethybridge, A. D.; Prue, J. E.; Spiers, D. J. *J. Solution Chem.* **1974**, *3*, 563. (b) Beronius, P. *Acta Chem. Scand. Ser. A* **1975**, *A29*, 289.

(24) (a) Justice, M. C.; Justice, J. C. *J. Solution Chem.* **1976**, *5*, 543. (b) Burg, R.; Justice, J. C. *Ibid.* **1977**, *6*, 349.

(25) (a) Hirsch, E.; Fuoss, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 1018. (b) Sadek, H.; Fuoss, R. M. *Ibid.* **1954**, *76*, 5905. (c) Gleysteen, L. F.; Kraus, C. A. *Ibid.* **1947**, *69*, 451. These data were recalculated by using the Fuoss–Hsia equation.
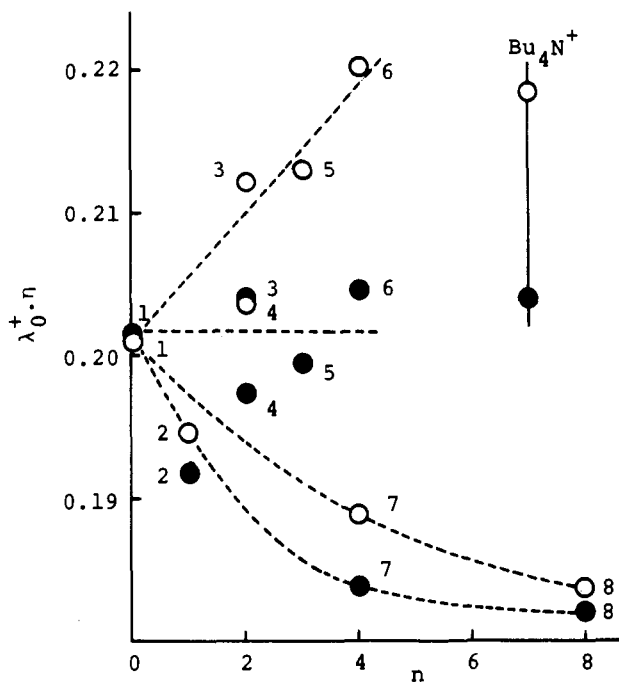
Figure 1. Walden products of [Co(acac)$_2$(diamine)]$^+$ as a function of the increased carbon number n compared to [Co(acac)$_2$(en)]$^+$ (data for Bu$_4$N$^+$ shown as reference): O, in PhNO$_2$; ●, in 1,2-DCE. Diamine: 1, en; 2, pn; 3, N,N-dmen; 4, N,N'-dmen; 5, N,N,N'-trimen; 6, N,N,N',N'-tmen; 7, 2-ampy; 8, bpy.

Table IV. Visible Spectra ($^1A_{1g} - {}^1T_{1g}$) of [Co(acac)$_2$(diamine)]ClO$_4$ in Nitrobenzene and 1,2-Dichloroethane^a

	nitro-benzene	1,2-dichloro-ethane
[Co(acac)$_2$(en)]ClO$_4$	546 (187)	549 (174)
[Co(acac)$_2$(pn)]ClO$_4$	545 (185)	549 (171)
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	557 (154)	559 (151)
[Co(acac)$_2$(N,N-dmen)]ClO$_4$	566 (161)	569 (155)
[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$	575 (143)	577 (141)
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$	597 (133)	601 (130)

^{a} The peak position is given in nm with the molar extinction coefficient value (ϵ) indicated in parentheses.

Although the transference number is not available, the limiting conductances (λ_0^+) and Walden products ($\lambda_0^+\eta$) of the chelate cations are obtained from the limiting conductances of the perchlorate ion, λ_0^+(ClO$_4^-$) = 20.9[26] and 39.2[27] in PhNO$_2$ and 1,2-DCE, respectively (Table III). The association constants for the perchlorate are smaller than those for the iodide (Tables I and II) and bromide,[13] and the hydration of the ClO$_4^-$ ion by a small amount of water in these solvents is negligible compared to that of the halide ions.[28] Thus, the perchlorates are preferred for obtaining the accurate limiting conductances of the chelate cations.

Discussion

(a) Mobilities of the [Co(acac)$_2$(diamine)]$^+$ Ions. In Figure 1 the Walden products of the [Co(acac)$_2$(diamine)]$^+$ ion in PhNO$_2$ and 1,2-DCE are plotted against the carbon number of the substituents in [Co(acac)$_2$(diamine)]$^+$. (1) The λ_0^+ values of the chelate cations with the N-methylated diamine in PhNO$_2$ increase gradually with the number of methyl groups while the dependence in 1,2-DCE is not clear. (2) The difference in the Walden product of [Co(acac)$_2$(en)]$^+$, [Co-(acac)$_2$(pn)]$^+$, and [Co(acac)$_2$(bpy)]$^+$ between PhNO$_2$ and 1,2-DCE is significantly smaller than that of [Co(acac)$_2$-(N,N,N',N'-tmen)]$^+$ and Bu$_4$N$^+$.

The [Co(acac)$_2$(diamine)]$^+$ ions are larger than the solvent molecules. Therefore, the behavior of mobility should follow hydrodynamic theories such as Stokes' law, which states that the larger the crystallographic radius, the smaller the mobility. The molal volume of the chelate cations is increased with N-methylation due to the increase in volume with the introduction of CH$_3$ groups. In addition, the conformation change may occur through the steric hindrance between the coordinated acac and the N-methylated diamine. As is shown in Table IV, the absorption peaks of $^1A_{1g} - {}^1T_{1g}$[20] in both PhNO$_2$

and 1,2-DCE are red shifted with the N-methylation. This indicates that the Co–N bond distance is lengthened by the introduction of the N-methyl groups, in opposition to the prediction from the inductive effect of N-methyl groups. Consequently, the molal volume of the chelate cations would further increase with the N-methylation, owing to the increase in the Co–N bond distance.

Thus, result 1 conflicts with hydrodynamic theory, suggesting specific ion–solvent interaction. Both solvents are poorly basic, and PhNO$_2$ is greatly dipolar (μ = 4.27) while 1,2-DCE is poorly so (μ = 1.19). The chelate cation [Co-(acac)$_2$(en)]$^+$ has a solvated site; that is, polar solvent molecules approach the NH group side because of its asymmetric structure. Especially, it is likely that polar nitrobenzene solvates the chelate cation due to the ion–solvent dipole interaction. The introduction of N-methyl groups promotes the desolvation, leading to the increase in mobility due to the decrease in its effective size, in marked contrast to ionic conductivities of a homologous series of butylammonium ions in nitrobenzene (NH$_4^+$, 18.4; BuNH$_3^+$, 17.0; Bu$_2$NH$_2^+$, 14.4; Bu$_3$NH$^+$, 12.9; Bu$_4$N$^+$, 11.8),[26] which is attributed to the bulkiness of butyl groups. On the other hand, the result of [Co(acac)$_2$(diamine)]$^+$ in 1,2-DCE, which is a lower dielectric solvent, suggests that the increase in mobility due to the desolvation accompanying the N-methylation is comparable to the decrease in mobility due to the volume increase of the cation itself. In contrast to the cations with the N-methylated diamine, the mobility of the pn cation is smaller than that of the en cation in both solvents, being attributed to the volume increase by the methyl group without the desolvation effect. For the pyridine derivatives, the size of the cation increases in the order [Co(acac)$_2$(en)]$^+$ < [Co(acac)$_2$(2-ampy)]$^+$ < [Co(acac)$_2$(bpy)]$^+$ because of bulky aromatic ligands, conforming to mobility data.

In regard to result 2, the Zwanzig equation[29] predicts that the ionic Walden products will decrease with decreasing dielectric constant (D) from PhNO$_2$ (D = 34.82) to 1,2-DCE (D = 10.36). This is the case for Bu$_4$N$^+$ in Table III (the difference in Walden products 0.014). The similar Walden products of [Co(acac)$_2$(en)]$^+$ and [Co(acac)$_2$(pn)]$^+$ in both solvents can be, thus, attributed to the decrease in mobility of the en and pn cations in PhNO$_2$ due to the specific interaction between the NH groups and PhNO$_2$. On the other hand, although both [Co(acac)$_2$(bpy)]$^+$ and [Co(acac)$_2$($N,-N,N',N'$-tmen)]$^+$ cations have no NH protons, they show mobility behavior different from each other. The behavior of [Co(acac)$_2$(bpy)]$^+$, although similar to that of [Co(acac)$_2$-(en)]$^+$, may be ascribed to the π–π interaction between nitrobenzene molecules and the aromatic bpy ligand. This interaction has already been observed for the optical resolution of [Co(acac)$_3$] and [Cr(acac)$_3$] by optically active [Ni-(phen)$_3$]$^{2+}$[5] and the conductivity of pyridinium salts in pyr-

(26) Witschonke, C. R.; Kraus, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 2472.

(27) Kraus, C. A. *J. Chem. Educ.* **1958**, *35*, 324.

(28) (a) Yamamoto, Y.; Tarumoto, T.; Tarui, T. *Bull. Chem. Soc. Jpn.* **1974**, *46*, 1466. (b) Kenjo, T.; Diamond, R. M. *J. Inorg. Nucl. Chem.* **1974**, *36*, 183.

(29) (a) Zwanzig, R. *J. Chem. Phys.* **1963**, *38*, 1603. (b) Zwanzig, R. *Ibid.* **1970**, *52*, 3625.
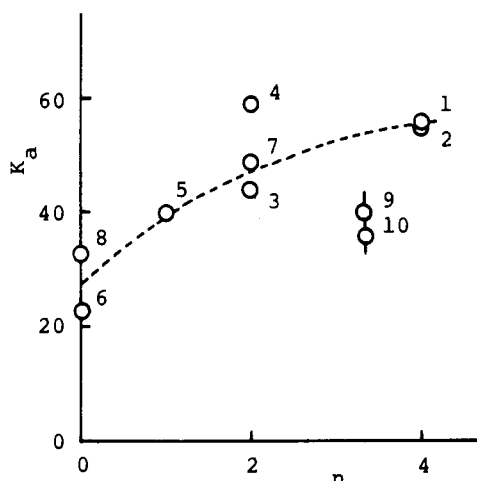
Figure 2. K_a of [Co(acac)$_2$(diamine)]ClO$_4$ as a function of the number of the NH protons n in the chelate cations in PhNO$_2$. Numbers are the same as in Figure 1 except for 9, Bu$_4$NClO$_4$, and 10, Et$_4$NClO$_4$.
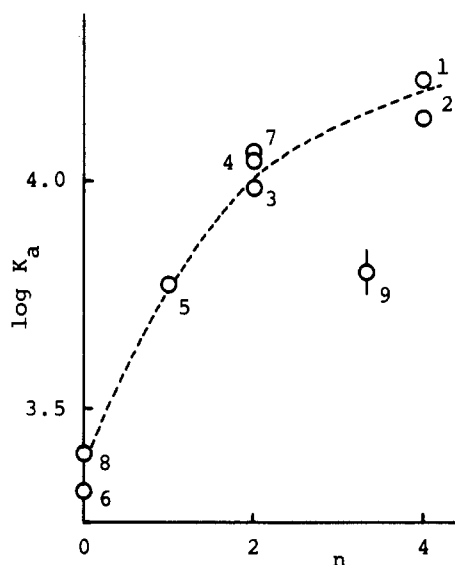

Figure 3. log K_a of [Co(acac)$_2$(diamine)]ClO$_4$ as a function of the number of the NH protons n in the chelate cations in 1,2-DCE. Numbers are the same as in Figure 2.

idine–nitrobenzene solvents.[18e] However, this effect was not obtained for the acac ligand with aromaticity in [Co(acac)$_2$-(diamine)]$^+$ as is clear from the data of [Co(acac)$_2$($N,N,-N',N'$-tmen)]$^+$, probably due to the weaker aromaticity.

(b) Ionic Association of [Co(acac)$_2$(diamine)]X. Figures 2 and 3 show that (1) Ionic association constants (K_a) of [Co-(acac)$_2$(diamine)]ClO$_4$ in PhNO$_2$ and 1,2-DCE decrease with the decrease in the number of the NH protons in the chelate cations and the contribution to K_a per NH proton is larger in 1,2-DCE than in PhNO$_2$ and (2) K_a of the N,N'-dmen complex in PhNO$_2$ is somewhat larger than that of the en complex in spite of decreasing the number of the N–H protons, in contrast to that in 1,2-DCE.

(1) As the chelate cations, which consist of the mixed ligands, possess the asymmetry in the charge distribution, anion–cation dipole interaction should promote a degree of association by the short-range interaction to the ClO$_4$$^-$ ion through the NH protons of the diamine in the chelate cations.

The magnitude of association constants can be evaluated for ions in a continuous dielectric medium by using the Fuoss[30a] and Bjerrum[30b] equations. For ions with polarity, such as

[Co(NH$_3$)$_5$(NO$_2$)]$^{2+}$,[31] in addition to the energy term for the equations, $E = e^2/rDkT$, the term for ion–dipole interaction, $E_1 = \mu e/r_1^2 DkT$, should be imposed, where μ is the dipole moment of the chelate cations and r and r_1 are the distances from the center and dipole center of the cation to the anion, respectively. If μ is taken as 6 D[31] and $r = r_1 = 5$ Å[32] for [Co(acac)$_2$(diamine)]ClO$_4$, E_1 is 24% of E, increasing K_a 2.2 and 1.7 times for the Fuoss and Bjerrum equations, respectively. Thus, the effect of E_1 is not negligible. However, it seems unlikely that the introduction of substituents leads to the large change in the polarity of the chelate cations compared to that of the [Co(acac)$_2$(en)]$^+$ ion. Moreover, the K_a values of [Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$ and [Co(acac)$_2$-(bpy)]ClO$_4$ in both solvents are smaller than that of Bu$_4$NClO$_4$, which is roughly equal in size to the N,N,N',N'-tmen complex hydrodynamically, in spite of the enhancement effect of the dipole moment of the chelate cations on K_a. This suggests that when there is no hydrogen bond, the acac ligand with the pseudoaromaticity and the aromatic bpy reduce the ion-pair formation, probably due to the repulsion between ClO$_4$$^-$ and the π electron of the ligands and the distribution of positive charge through the coordination bonds.[9,13] Thus, although the solvation of the NH protons by nitrobenzene molecules occurs (Figure 1), the ion pair in PhNO$_2$ must be a contact ion pair, formed by partial exclusion of nitrobenzene molecules. This is confirmed from the fact that the ratio of K_a of [Co(acac)$_2$(en)]ClO$_4$ to [Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$ in PhNO$_2$ is 2.4 and is much smaller than that of 1,2-DCE (7.9). Further, this trend is valid for the other chelate complexes with NH protons.

The strength of the hydrogen bond between the NH protons and anions increases in the order ClO$_4$$^-$ < I$^-$ < Br$^-$. However, the K_a values of [Co(acac)$_2$(en)]X (X$^-$ = I$^-$, Br$^-$) in both solvents are much smaller than those of Bu$_3$NHI (1.05 × 10^4)[26] and Et$_3$NHBr (1.64 × 10^5)[18a] in PhNO$_2$ and of Bu$_3$NHI (6.4 × 10^7)[17a] and Bu$_3$NHBr (1.2 × 10^9)[17a] in 1,2-DCE. Although the charge of Bu$_3$NH$^+$ is localized on the NH group, the positive charge of [Co(acac)$_2$(en)]$^+$ is distributed over the aromatic ligand (acac) far from the NH group. Therefore, the acidity of the NH protons in [Co(acac)$_2$(en)]$^+$ may be reduced, leading to the lower association constant.

(2) It has been shown that the alkyl substitution (CH$_3$NH– and –CH$_2$NH$_2$) in the coordinated amine results in more acidity of the residual NH protons, from the studies of the rate of H–D exchange[33] and the acid ionization constant[34] in aqueous solutions. The effect of the acidity of the NH protons on the ionic association was observed:[13] K_a (=749) of [Co-(acac)$_2$(N,N'-dmen)]Br in PhNO$_2$ is much larger than that (449) of [Co(acac)$_2$(en)]Br in spite of the decrease in the number of NH protons for hydrogen bonding with the Br$^-$ ion. We have interpreted the source of the "activation" in terms of preventing solvation of the residual NH protons because of the steric hindrance by the nearest-neighbor CH$_3$ groups. In this study, K_a of [Co(acac)$_2$(N,N'-dmen)]ClO$_4$ is larger than that of [Co(acac)$_2$(en)]ClO$_4$ in nitrobenzene although the difference is small due to the weaker hydrogen bond ability of the ClO$_4$$^-$ ion. On the other hand, the reverse trend was observed for 1,2-DCE. The activation of the NH protons in 1,2-DCE due to the desolvation effect by the N-methyl sub-

(30) (a) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059. (b) Bjerrum, N. K. *Dan. Vidensk. Selsk. Skr., Naturvidensk. Math. Afd.* **1926**, *7*, 9.

(31) Masterton, W. L.; Bierty, T. *J. Solution Chem.* **1976**, *5*, 721. The dipole moment of the [Co(NH$_3$)$_5$(NO$_2$)]$^{2+}$ ion was estimated to be in the vicinity of 6 D from conductance data.

(32) Matsumoto, K.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3307. The X-ray study of (–)$_{589}$-[Cr(acac)$_2$(tn)]I·H$_2$O (tn = 1,3-propanediamine) indicated that the interionic distance Cr–I is 5.03 Å.

(33) (a) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 1790. (b) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Ibid.* **1979**, *18*, 2041.

(34) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

stitution is small, since the solvation of the NH protons by 1,2-dichloroethane is weaker than that by nitrobenzene. Therefore, K_a of the N,N'-dmen complex in 1,2-DCE becomes smaller compared to that of the en complex, in contrast to the result in PhNO$_2$. Thus, the K_a values of the chelate electrolyte in 1,2-DCE decrease with the decrease in the number of NH protons, monotonously.

In conclusion, the difference in the conductance behavior of [Co(acac)$_2$(diamine)]ClO$_4$ in PhNO$_2$ and 1,2-DCE can be interpreted in terms of specific ion–solvent interactions involving hydrogen bonding through the NH protons, its activation by the introduction of the N-methyl groups in PhNO$_2$, and the π–π interaction between the bpy ligand and nitrobenzene molecules. Particularly, the difference in both solvents could be monitored from mobility data.

Crystal Structure and Magnetic Properties of (μ-Azido)(μ-hydroxo)bis[(N,N,N',N'-tetramethylethylenediamine)copper(II)] Perchlorate, a Copper(II) Dinuclear Complex with a Large Ferromagnetic Interaction

OLIVIER KAHN,*[1a] SONIA SIKORAV,[1a] JACQUELINE GOUTERON,[1b] SUZANNE JEANNIN,[1b] and YVES JEANNIN*[1b]

Received February 10, 1983

The title compound has been synthesized and its structure has been solved at room temperature. It crystallizes in the tetragonal system, space group $P4_2/mnm$. Its lattice constants are $a = b = 9.50 \pm 0.02$ Å and $c = 13.94 \pm 0.03$ Å with $Z = 2$. The structure consists of [Cu$_2$(tmen)$_2$(N$_3$)(OH)]$^{2+}$ dinuclear cations and perchlorate anions. In each cationic unit, the copper(II) ions are four-coordinated with planar surroundings; they are bridged by an azido group in an end-on fashion and by a hydroxo group. The bridging network is disordered. The Cu–N$_{P_1}$ distance is 1.960 (9) Å, and the Cu–N$_{P_1}$–Cu angle is 99.4 (6)°, N$_{P_1}$ being the N$_{0.5}$O$_{0.5}$ composite bridging atom. The magnetic properties of the title compound have been investigated in the 2–300 K temperature range. $\chi_M T$, the product of the molar magnetic susceptibility and the temperature, is equal to 1.02 cm^3 mol^{-1} K at 295 K, increases up to 1.15 $\pm$ 0.02 cm^3 mol^{-1} K at 150 K, and then remains constant down to 20 K. This behavior shows that the ground state is the spin triplet and that the excited spin singlet state is so high in energy that it is only weakly populated, even at room temperature. This singlet–triplet energy gap is estimated to be larger than 200 cm^{-1}. The specific ability of the end-on azido bridge to favor the triplet state in dinuclear copper(II) complexes is emphasized. An interpretation based on a spin polarization effect is proposed. The magnetic properties of the title compound are compared to those of [Cu(tmen)(N$_3$)$_2$]$_2$, where the two copper(II) ions are noncoupled.

Introduction

Until now, two strategies have been described to achieve a ferromagnetic interaction between two metal ions belonging to the same molecular entity, namely the strict orthogonality or the accidental orthogonality of the magnetic orbitals.[2]

The strict orthogonality occurs when the magnetic orbitals around a metal center transform as the Γ_i irreducible representations of the molecular symmetry group, and the magnetic orbitals around the other metal center transform as Γ_j with $\Gamma_i \neq \Gamma_j$ for any i and j. These conditions are realized in Cu^{II}VO^{II} and Cu^{II}Cr^{III} heterobinuclear complexes.[2,3] The accidental orthogonality between two magnetic orbitals ϕ_A and ϕ_B of the same symmetry, characterized by $\langle \phi_A | \phi_B \rangle = 0$, can occur for very peculiar values of the structural parameters.

In this case, around each bridge, the positive lobes of the overlap density $\rho(i) = (\phi_A(i))(\phi_B(i))$ exactly compensate the negative lobes.[4] It has been shown that this accidental orthogonality could be realized in planar dinuclear copper(II) complexes like 1.[4-7] Thus, when Y is a nitrogen atom of a

1
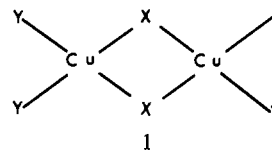
diamine and X is the hydroxo group, the accidental orthogonality is expected for a value of the bridging angle close to 90°.

(1) (a) Université de Paris Sud. (b) Université Pierre et Marie Curie.
(2) Kahn, O. *Inorg. Chim. Acta* 1982, 62, 3 and references therein.
(3) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* 1982, 104, 2165. Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J.; Jaud, J. *J. Am. Chem. Soc.*, in press.
(4) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* 1980, 4, 567.
(5) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. J. *J. Am. Chem. Soc.* 1975, 97, 4884.
(6) Crawford, V. M.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* 1976, 15, 2107.
(7) Hodgson, D. J. *Inorg. Chem.* 1976, 15, 3174.