

neutral ligand donor orbitals. The relative amount of metal-neutral ligand covalent bonding depends upon the stability of the MX_2 acceptor valence orbitals, *i.e.*, energy match of L and appropriate cobalt(II) orbitals. As the energy of the MX_2 acceptor valence orbitals of the MX_2 group increases, the covalent bonding with the neutral ligand decreases. Application of the MO bonding model leads to the prediction that the energy (destabilization) of the MX_2 acceptor orbitals increases in the order $\text{MCl}_2 > \text{MBr}_2 > \text{MI}_2$ (Figures 1 and 2). The magnitude of the metal-neutral ligand covalent bonding is thus expected to increase in the order $\text{CoL}_2\text{Cl}_2 < \text{CoL}_2\text{Br}_2 < \text{CoL}_2\text{I}_2$. This result agrees with the increase in ligand proton contact shifts when the anion is changed from Cl^- to Br^- to I^- .

The bonding properties of thiocyanate are almost certainly affected by $d\pi-p\pi$ back-bonding (from the metal d to the thiocyanate π MO). The very large Dq for thiocyanate (N-bonded) toward T_d Co(II) can best be explained in terms of the lowering of the filled metal d orbitals (the e set) due to back-donation into the antibonding π orbitals of thiocyanate. The large neutral ligand contact shift in the thiocyanate complex is consistent with increased effective charge on the metal that would result from back-bonding.

Conclusions from a comparison of $\text{Co}(\text{HMPA})_2(\text{NO}_3)_2$ with the halide complexes have to be qualified because of the uncertainty in the symmetry of $\text{CoL}_2(\text{NO}_3)_2$ in solution. Bidentate nitrate has been found¹⁶ in similar complexes in the solid state. If, as previously proposed,¹⁶ the immediate environment about the cobalt has, in a sense, "distorted tetrahedral symmetry," the pseudo-contact term may be small and comparison of the contact shift of the complex with the

halide complexes legitimate. According to the data in Table I, nitrate would be located between iodide and thiocyanate. This is reasonable for nitrate would not be expected to form strong covalent bonds. Since back-bonding from metal to nitrate would not be expected to be very large, the large contact shift in this complex is attributed to a lesser degree of covalency in the metal-nitrate bond than in the metal-chloride bond.

Comparison of the contact shifts for $\text{Co}(\text{HMPA})_4^{2+}$ and $\text{Co}(\text{HMPA})_2\text{Cl}_2$ indicates that HMPA does not decrease the charge on cobalt as much as chloride or bromide.

The conclusion of the above discussion can be generalized to rationalize some of the halogen effects in other chemical species. The order for the C-H stretching force constants in CH_3X is $\text{F} < \text{Cl} < \text{Br} < \text{I}$.¹⁵ The order of C-X bond energies is $\text{I} < \text{Br} < \text{Cl} < \text{F}$.¹⁷ The C-H force constants thus decrease as the C-X bond energy increases. These data may reflect the trend in destabilization of the carbon orbitals used in bonding with hydrogen as the C-X bond energy increases. The increase in the enthalpy for formation of $\text{Co}(\text{py})_4\text{X}_2$ from $\text{Co}(\text{py})_2\text{X}_2$ ¹⁸ as the anion is changed from Cl^- to Br^- to I^- is also consistent with these arguments.

Acknowledgment. The authors acknowledge partial support of this research by the Chemistry Branch of the Atomic Energy Commission through Contract No. AT(11-1)-758.

(17) W. J. Linnett, *Quart. Rev. (London)*, **1**, 73 (1947).

(18) H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

Investigations of the Cobalt(II) Complexes of N,N-Dimethylacetamide

Bradford B. Wayland,^{1a} Ronald J. Fitzgerald,^{1b} and Russell S. Drago

Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois Received December 27, 1965

Abstract: Complexes with the formulas $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ have been isolated. Infrared spectral and conductance data are presented to eliminate the possibility of perchlorate coordination in $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$. Parameters obtained from the electronic spectra and magnetic moments indicate approximate tetrahedral and octahedral ligand fields for the four- and six-coordinate complexes, respectively. Vibrational spectra demonstrate coordination through the DMA carbonyl oxygen for both complexes. Simultaneous coordination through both the carbonyl oxygen and amide nitrogen may be present in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ or distortion from pure T_d symmetry may result from ion pairing. The crystal-field prediction that $Dq(\text{tetrahedral})/Dq(\text{octahedral}) = 0.44$ is found not to agree with our experimental results, and possible explanations are offered. The nmr contact shifts of the octahedral and tetrahedral complexes indicate more covalency in the tetrahedral complex.

The preparation and isolation of mixed neutral ligand-anion complexes of a metal ion in two different symmetries is well known. The best known examples of this type of complex are the four-coordinate Co-

$(\text{py})_2\text{X}_2$ and the six coordinate $\text{Co}(\text{py})_4\text{X}_2$ (py = pyridine, X = halide).^{2,3} Tetrahedral and octahedral environments for nickel(II)⁴ and cobalt(II)⁵ metal ions

(2) H. C. King, E. K v s, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(3) S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

(4) R. Pappalardo, D. L. Wood, and R. C. Linares, *J. Chem. Phys.*, **35**, 1460 (1961).

(1) (a) Abstracted in part from the Ph.D. thesis of B. Wayland, University of Illinois, 1964; NSF Graduate Fellow, 1963-1964; (b) abstracted in part from the Ph.D. Thesis of R. Fitzgerald, University of Illinois, 1968.

introduced into ZnO and MgO lattices have also been reported. Forster and Goodgame have recently reported a series of anion complexes where a single metal ion and anion form both tetrahedral and octahedral complexes.^{6,7} The presence of both a tetrahedral and an octahedral complex of cobalt(II) containing only water as the ligand has been proposed in the aqueous solution of $\text{Co}(\text{NO}_3)_2$ on the basis of kinetic measurements.⁸ No report of the isolation of these or analogous complexes has been made. Transition metal ion complexes with different numbers of the same neutral ligand as the only coordinated species are very rare.

This paper reports the first definite isolation of complexes of the form $[\text{CoL}_4](\text{ClO}_4)_2$ and $[\text{CoL}_6](\text{ClO}_4)_2$, where L is the only coordinated species and is a neutral ligand. The neutral ligand used in this investigation is N,N-dimethylacetamide (DMA). Magnetic and electronic spectral data indicate that Co(II) experiences an approximately tetrahedral ligand field in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ and an octahedral ligand field in $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$. Vibrational spectra and conductance data are used to indicate the absence of perchlorate anion coordination in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$. Calculations made on the basis of regular symmetry for these complexes give the ratio $\Delta(\text{tetrahedral})/\Delta(\text{octahedral}) = 0.64$. This experimental ratio may be compared with the value 0.44 predicted by crystal-field theory.^{9,10} Possible reasons for this deviation are discussed.

Experimental Section

1. Apparatus. The nmr spectra were obtained with both Varian Model A-60 and Varian Model DP-60 nmr spectrometers. All nmr spectra were measured relative to tetramethylsilane (TMS) as an internal standard.

All near-infrared, visible, and ultraviolet spectra were determined using a Cary Model 14M recording spectrophotometer.

The magnetic susceptibilities were measured at 28° using a Gouy magnetic balance. The Gouy tubes were calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$.¹¹ The measured susceptibilities were corrected for diamagnetism by use of Pascal's constants.¹¹ The solution moment was determined at 34.5° by nmr using a method first reported by Evans.¹²

Infrared spectra were determined using a Perkin-Elmer grating infrared spectrophotometer, Model 521.

The conductance measurements were made on an Industrial Instruments conductivity bridge, Model RC 16B2.

2. Preparation of Complexes. (a) $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$. Anhydrous CoCl_2 (1.50 g) was added to a solution of 4.77 g of anhydrous AgClO_4 in N,N-dimethylacetamide (DMA). The nonhomogenous mixture was stirred at room temperature for 24 hr. Silver chloride was removed by filtration and centrifugation of the solution. Addition of anhydrous ether to the solution precipitated a pink-violet complex which was redissolved in N,N-dimethylacetamide, centrifuged to remove traces of AgCl , and then reprecipitated by addition of ether. The solution was then filtered in a drybox and washed *once* with ether. The extremely hygroscopic pink-violet complex resulted. *Anal.* Calcd for $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$: C, 36.9; H, 6.9; N, 10.8. Found: C, 36.7; H, 7.0; N, 10.6.

(5) R. Pappalardo, D. L. Wood, and R. C. Linares, *J. Chem. Phys.*, **35**, 2041 (1961).

(6) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).

(7) D. Forster and D. M. L. Goodgame, *ibid.*, **4**, 1712 (1965).

(8) T. J. Swift, *ibid.*, **3**, 526 (1964).

(9) L. E. Orgel, "An Introduction to Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p 25.

(10) C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 110.

(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 440-454.

(12) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(b) $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$. The four-coordinate complex of Co(II) with DMA was made from the six-coordinate complex by recrystallization from either CH_2Cl_2 or CHCl_3 . Repeated washing of the six-coordinate complex with ether also eventually yielded the deep blue four-coordinate cobalt(II) complex. This complex is also very hygroscopic. *Anal.* Calcd for $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$: C, 31.7; H, 5.99; N, 9.24. Found: C, 31.4; H, 5.82; N, 9.11.

3. Reagents and Solutions. "Anhydrous" silver perchlorate from the G. F. Smith Co. was used without purification. Cobalt(II) chloride was dried by heating in an oven at 120° for 48 hr. Fisher reagent grade N,N-dimethylacetamide was distilled from BaO twice under a reduced pressure of approximately 30 mm. Anhydrous reagent grade diethyl ether was used without further purification.

All solutions of hygroscopic materials were prepared in a drybox equipped with an automatic continuous air-flow drying system. When accurate complex or ligand concentrations were necessary, materials were weighed in stoppered volumetric flasks.

Results

The spectral data for the complexes are contained in Table I along with assignments for the transitions. For the tetrahedral cobalt(II) complex, a β value of

Table I. Spectral Bands for $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$

Compound	Solvent	ν_{max} , cm^{-1}	ϵ_{max} , cm^{-1} mole	Band assignment
$[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$	DMA	6,870	3.0	${}^4\text{T}_1(\text{F}) \rightarrow \text{T}_2(\text{F})$
		13,700	1.0	$\rightarrow \text{}^4\text{A}_2(\text{F})$
		18,380	20.5	$\rightarrow \text{}^4\text{T}_1(\text{P})$
		20,830	10.0	
$[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$	CH_2Cl_2	6,500	13.0	${}^4\text{A}_2(\text{F}) \rightarrow \text{}^4\text{T}_1(\text{F})$
		8,278	19.3	
		10,580	10.7	
		16,340	95.0	${}^4\text{A}_2(\text{F}) \rightarrow \text{}^4\text{T}_1(\text{P})$
		17,182	110.5	
		18,587	79.4	

0.82 and oscillator strengths of 1.43×10^{-4} and 1.51×10^{-3} were obtained for the low-energy and high-energy transitions, respectively.

The molar absorptivity of $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ in CH_2Cl_2 is low for a tetrahedral complex. However, it was found that there is no difference in this value for solutions of the complex varying in concentration from 0.005 to 0.05 M. It was also found that addition of a threefold molar excess of DMA has no effect on the observed spectra. These results suggest that the predominant species in solution is $\text{Co}(\text{DMA})_4^{2+}$.

Magnetic susceptibility data are included in Table II.

The results of the nmr studies are contained in Table III. The quantity $\Delta\nu$ is the shift of the resonance of coordinated DMA relative to free DMA. The subscripts a, b, and c correspond to the methyl hydrogens denoted a, b, and c in the planar DMA molecule of Figure 1. The table indicates the assignment of the peaks in the spectrum to the respective hydrogens in the amide. These assignments for the octahedral complexes were made by successively adding small increments of the complex to DMA as the solvent and observing the shifted resonances. The resonances in the complex can be traced back to their sources in the ligand in this manner. A similar technique was used for $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$, except that DMA was added to a CH_2Cl_2 solution of the complex. Since rapid exchange occurs at room temperature, only a single peak is

Table II. Magnetic Susceptibility Data for [Co(DMA)₆](ClO₄)₂ and [Co(DMA)₄](ClO₄)₂

Complex	10 ⁶ χ _m	10 ⁶ χ (diamag)	10 ⁶ χ _m ^{corr}	μ _{eff} , BM	State ^a
[Co(DMA) ₆](ClO ₄) ₂	10,350	-360	10,710	5.08 ± 0.05	Solid
[Co(DMA) ₄](ClO ₄) ₂	8,767	-252	9,019	4.68 ± 0.05	Solid
[Co(DMA) ₄](ClO ₄) ₂	8,387	-252	8,639	4.63 ± 0.05	Solution

^a Solid moments determined at 28°, solution moment at 34.5°.

Table III. Nmr Spectra of Four- and Six-Coordinate Complexes^a

Complex	Δν _a	Δν _b	Δν _c	Solvent
Co(DMA) ₆ (ClO ₄) ₂	-262	-649	+44	DMA
Ni(DMA) ₆ (ClO ₄) ₂	-122	-261	+182	DMA
Co(DMA) ₄ (ClO ₄) ₂	-1021	-1017	-342	CH ₂ Cl ₂
Co(DMA) ₄ (ClO ₄) ₂	-995	-1103	...	CH ₃ NO ₂

^a Δν in units of cps relative to the respective resonance position in the uncomplexed ligand.

observed for each of these hydrogens (*i.e.*, separate complex and solvent resonances are not detected). The values reported in Table III for Δν were calcu-

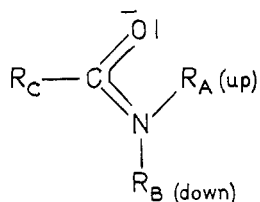


Figure 1. Labeling of the methyl protons in N,N-dimethylacetamide.

lated from the equation Δν_{obsd} = (mole fraction complexed)(Δν complexed).

Conductance data are presented in Table IV.

Table IV. Conductance Data for Various Complexes in CH₂Cl₂

Complex	Type	Λ _{molar}	Temp, °C	Concn × 10 ³ , M
[Ni(py) ₄](ClO ₄) ₂ ^a	Nonionic	1.72	22.4	0.292
[Ni(py) ₅ (NO ₃) ₂] ^a	Nonionic	0.194	22.6	0.324
[Ni(py) ₄ (H ₂ O) ₂](ClO ₄) ₂ ^b	2:1	8.74	24.0	1.04
[Co(DMA) ₄](ClO ₄) ₂	2:1	12.1	26.1	4.12

^a Unpublished results from the Ph.D. thesis of M. Rosenthal, University of Illinois, 1965. ^b Conductance run on the complex prepared according to M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **5**, 492 (1966).

Discussion

1. Structures of the Complexes. The possibility of perchlorate coordination in [Co(DMA)₄](ClO₄)₂ may be eliminated on the basis of the infrared spectrum and conductance data. The infrared spectrum of [Co(DMA)₄](ClO₄)₂ in CDCl₃ in the range 1200–900 cm⁻¹ contains a broad peak, with a maximum at 1100 cm⁻¹ which is characteristic of uncoordinated perchlorate. Hathaway and Underhill¹³ have shown that monodentate coordinated perchlorate has two relatively

(13) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

narrow intense bands in the 1200–1000-cm⁻¹ region, while ionic perchlorate has a single broad peak. There is a small shoulder on the band in this complex which could be due to a slight perturbation of the T_d symmetry of perchlorate by ion pairing in solution. Clearly, however, the two narrow intense bands that are expected for the C_{3v} symmetry of monodentate perchlorate are not present. Conductance data, presented in Table IV, clearly indicate that [Co(DMA)₄](ClO₄)₂ is an electrolyte and thus the perchlorate cannot be coordinated.

The magnetic moment for crystalline [Co(DMA)₆](ClO₄)₂ is in the range expected for octahedral Co(II).¹¹ The solid and solution magnetic moments for [Co(DMA)₄](ClO₄)₂, although slightly larger than expected for the observed Δ value, are consistent with an approximate tetrahedral ligand field.^{14,15}

The electronic spectra (Table I) for [Co(DMA)₄](ClO₄)₂ and [Co(DMA)₆](ClO₄)₂ compare favorably with spectra previously reported for tetrahedral¹⁵ and octahedral¹⁶ Co(II) complexes. As previously noted the molar absorptivities of [Co(DMA)₄](ClO₄)₂ in CH₂Cl₂ are somewhat lower than are generally found for tetrahedral complexes. However, the oscillator strength $f(\nu_3)$ fits a previously reported¹⁷ plot of ΔB *vs.* $f(\nu_3)$. The fit is as good as that reported for [CoCl₄]²⁻, [CoBr₄]²⁻, and [CoI₄]²⁻. The electronic spectra and magnetic properties for [Co(DMA)₄]²⁺ are reminiscent of those for [Co(NO₃)₄]²⁻.^{18,19} Both complex ions have slightly larger magnetic moments, lower absorptivities, and larger Δ values than expected. The structure of [Co(NO₃)₄]²⁻ has recently been shown to have eight oxygens surrounding the Co(II).²⁰ Each cobalt-nitrate ion bond system consists of one relatively short Co–O bond and a longer Co–O bond. The net effect of the eight nitrate oxygens is to produce an approximate tetrahedral field about cobalt. Similarly, N,N-dimethylacetamide has two potential donor atoms bonded to a central carbon. The nitrogen may be capable of an interaction analogous to that of the “long” oxygen in [Co(NO₃)₄]²⁻. It is also possible that extensive ion pairing in solution causes a distortion in the complex similar to that produced from a ligand like nitrate ion.

The unusually large splitting of the ν₂ transition ⁴A₂(F) → ⁴T₁(F) for [Co(DMA)₄]²⁺ is also observed in Co(NO₃)₂²⁻ and could be due to a similar ligand field

(14) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **32**, 1168 (1960).

(15) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(16) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(17) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).

(18) D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

(19) F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.*, **84**, 2013 (1962).

(20) F. A. Cotton and J. G. Bergman, *ibid.*, **86**, 2941 (1964).

symmetry interaction in these two complexes. The splitting of the ν_2 band in the electronic spectra of "known tetrahedral" Co(II) complexes is frequently much larger than can be accounted for by spin-orbit coupling. This effect may arise from the dynamic Jahn-Teller effects in the excited states.¹⁵ Thus the large splitting of the ν_2 band for $[\text{Co}(\text{DMA})_4]^{2+}$ cannot be used to prove that a distortion from regular tetrahedral symmetry is present. Support for distortion from regular tetrahedral symmetry comes from a consideration of the spin-orbit coupling constant, λ' , for the tetrahedral Co(II) complex.

The spin-orbit coupling constants λ' for coordinated Co(II) are reduced in magnitude from that of the free ion value of -178 cm^{-1} . The spin-orbit coupling constant for a tetrahedral Co(II) complex may be calculated from the relationship $g = 2.00 - 8\lambda'/\Delta$,^{14,15} where g is obtained from magnetic measurements. Values determined from this relationship for known tetrahedral complexes are generally in the range of -130 to -160 cm^{-1} .¹⁵ The λ' value calculated from data^{18,19} for $\text{Co}(\text{NO}_3)_4^{2-}$ assuming tetrahedral symmetry is in the range -185 to -205 cm^{-1} , which is a larger negative number than the free-ion value. This improbable result must occur from the invalidity of using equations for tetrahedral complexes. The calculated λ' value for $[\text{Co}(\text{DMA})_4]^{2+}$ is in the range -200 to -220 cm^{-1} . This unreasonably large value for λ' most probably indicates that it is incorrect to treat the complex as rigorously tetrahedral. It is interesting that the complexes $\text{Co}(\text{tetramethylguanidine})_4(\text{ClO}_4)_2$ ²¹ and $\text{Co}(\text{ethylenethiourea})_4(\text{ClO}_4)_2$ ²² have calculated λ' values in the range -200 to -220 cm^{-1} . These ligands also have two potential donor sites. Thus, one may conclude that the ligand field symmetry in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ is to a first approximation respectively tetrahedral and octahedral. Deviations from expected behavior for tetrahedral Co(II) suggest that $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ is distorted from regular tetrahedral symmetry.

The shift in the DMA carbonyl vibrational frequency to lower frequency upon complexation is generally used to indicate coordination through the carbonyl oxygen.²³ The centers of intensity for the DMA carbonyl vibration in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ are respectively at 1606 and 1610 cm^{-1} . The carbonyl vibrational frequency for DMA in carbon tetrachloride is 1658 cm^{-1} . The carbonyl frequency shifts indicate that the carbonyl oxygen is the principal donor site but cannot be used to eliminate the possibility of simultaneous strong carbonyl oxygen coordination and weak nitrogen coordination. The solution of this problem must await a complete, single crystal X-ray analysis.

Nmr Contact Shifts. The nmr spectra of $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ each show two nonequivalent N-methyl resonances (Table III). Assignment of the ligand resonances is discussed in the Results section. The assignment of the methyl groups in the free ligand indicated that the N-CH₃ *cis* to the carbonyl is broader than the other N-CH₃.^{24,25} In

both complexes the broader N-methyl resonance is assigned to the N-methyl group pointed toward oxygen (*i.e.*, *cis* to the oxygen), and the broadest methyl resonance in the spectrum is assigned to the methyl group directly attached to the carbonyl group (Table III).

Isotopic nmr contact shifts result from the presence of unpaired spin density in the ligand molecular orbitals.^{26,27} Unpaired spin density arises in the ligand orbitals by covalent bonding with the paramagnetic metal ion. Contact shifts are sensitive to both the mode and extent of metal-ligand bonding.

The spin density distributions for DMA in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ and $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ are distinctly different (Table III). The different spin distributions reflect differences in the mode of bonding for the two complexes. These differences could result from the different metal ion electronic structures associated with tetrahedral and octahedral ligand fields. Another possibility is that a change in the nature of the coordination occurs. The larger N-methyl proton contact shifts in $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ compared with the octahedral complex could reflect nitrogen coordination or an increase in spin density in the π system of the ligand in the tetrahedral complex. Though the above effects complicate a rigorous interpretation of the contact shifts, the large differences in the magnitude of these shifts for the octahedral and tetrahedral complexes provide some of the best evidence to date for greater covalency in the tetrahedral complex than in the octahedral complex.

Spectrochemical Parameters. The Δ value for $[\text{Co}(\text{DMA})_6](\text{ClO}_4)_2$ is estimated to be $7600 \pm 400 \text{ cm}^{-1}$ from the Orgel diagrams published by Liehr for a d^7 case in an octahedral field.²⁸ This result is close to the value of 7690 cm^{-1} reported for the octahedral nickel(II) complex of DMA.²⁹ Ligand field calculations for Co(II) in a tetrahedral field have been extensively studied. The complex $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$, assuming tetrahedral symmetry, is calculated to have Δ equal to $4900 \pm 100 \text{ cm}^{-1}$, and B' equals 793 cm^{-1} . The same value is obtained by using frequencies from the center of intensity of the bands, and also by a weighting technique based on the theory of spin-orbit coupling for the excited states.^{30,31} The ratio $\Delta(T_d)/\Delta(O_h)$ is 0.64, compared to the value of 0.44 predicted by crystal-field theory. Forster and Goodgame^{6,7} have determined $\Delta(\text{tetrahedral})/\Delta(\text{octahedral})$ for the pairs of complexes $\text{Ni}(\text{NCS})_4^{2-}$ - $\text{Ni}(\text{NCS})_6^{4-}$ and $\text{Co}(\text{NCSe})_4^{2-}$ - $\text{Co}(\text{NCSe})_6^{4-}$, obtaining values of 0.51 and 0.49, respectively. There are several effects that should be considered when interpreting the large Δ ratio for the DMA complexes: (1) a steric effect in the octahedral complex, lowering $\Delta(O_h)$, (2) increased covalency in the tetrahedral complex, increasing $\Delta(T_d)$, and (3) potential bidentate donor properties of DMA, increasing $\Delta(T_d)$.

(24) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, (1960)

(25) C. Franconi, *Z. Elektrochem.*, **65**, 645 (1961).

(26) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(27) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

(28) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

(29) R. S. Drago, D. W. Meek, M. D. Joesten, and L. La Roche, *Inorg. Chem.*, **2**, 124 (1963).

(30) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(31) See, for example, J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 867 (1962).

(21) R. Longhi and R. S. Drago, *Inorg. Chem.*, **4**, 11 (1965) (magnetic data taken from ref 18 were corrected for temperature-independent paramagnetism).

(22) R. L. Carlin and S. L. Holt, Jr., *ibid.*, **2**, 849 (1963).

(23) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

There is good evidence available^{29,32} to indicate the existence of a steric effect in the octahedral Ni(DMA)₆²⁺ complex. The ease with which the octahedral cobalt complex is converted to the tetrahedral complex is probably partially due to the existence of steric effects in the six-coordinate complex. The attempted conversion of less sterically hindered [Co(DMF)₆](ClO₄)₂ to [Co(DMF)₄](ClO₄)₂ by the procedures described above was unsuccessful. This experiment offers some chemical evidence for the importance of the steric effect in the formation of [Co(DMA)₄]²⁺. The large ratio of $\Delta(T_d)/\Delta(O_h)$ is thus partially due to a steric effect lowering Δ in the octahedral complex.

The Δ value for DMA toward nickel(II) in the absence of a steric effect is estimated to be 8700 cm⁻¹ as an upper limit. This number is obtained by interpolation from the Δ 's for HC(O)NHCH₃ (8380 cm⁻¹), HC(O)N(CH₃)₂ (8500 cm⁻¹), and CH₃CONH₂ (8240 cm⁻¹). The value 8700 cm⁻¹ would give a $\Delta(T_d)$ to $\Delta(O_h^{cor})$ ratio of 0.56. In order to obtain the ratio 0.44, the Δ for DMA in the octahedral complex would have to have an unreasonably large value of 11,150 cm⁻¹. The lack of quantitative agreement between the adjusted experimentally determined ratio, 0.56, and the value predicted by crystal-field theory (0.44) requires that factors other than a steric effect contribute to the large ratio.

The larger Δ ratio is believed to be due in part to

(32) J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Maden, *Inorg. Chem.*, **4**, 18 (1965).

greater covalency in the tetrahedral compared to the octahedral complex. In addition to the evidence in the previous section to support this claim, Ballhausen and Liehr have shown semiquantitatively that electronic spectral intensities for d-d transitions are a direct function of the mixing of metal and ligand orbitals.³³ This conclusion has received support from the experimental observation that the measured oscillator strength for the d-d transition in tetrahedral Co(II) complexes is directly related to predicted metal-ligand covalency.¹⁷ A portion of the large ratio of tetrahedral to octahedral Δ observed experimentally in the DMA complexes may be due to a larger covalent σ interaction in the tetrahedral complex. The partially filled σ d orbitals are raised in energy by mixing with the filled σ ligand orbitals. This process would tend to split the metal d orbitals further, and d-d transitions would thus occur at higher energy. It is reasonable that there should be more effective covalent bonding in the tetrahedral complex, for ligand-ligand repulsions are decreased and effective metal ion charge is enhanced for the tetrahedral complex relative to the octahedral case.

A more detailed description of these interesting complexes must await the results of a complete structural analysis.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

(33) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 34 (1958).

Coordination Compounds with Delocalized Ground States. Bisdithiodiketone Complexes of Iron and Cobalt¹

G. N. Schrauzer,² V. P. Mayweg, H. W. Finck, and W. Heinrich

Contribution from the Institute of Inorganic Chemistry, The University, Munich, Germany, and, in part, Shell Development Company, Emeryville, California. Received June 10, 1966

Abstract: The preparation, properties and reactions of dithiodiketone complexes of iron and cobalt are reported. It is concluded that FeS₄C₄(CF₃)₄ as well as FeS₄C₄Ph₄ and CoS₄C₄Ph₄ are metal-sulfur bridged dimers M₂S₈C₈R₈ with structures analogous to that observed for Co₂S₈C₈(CF₃)₈. Thermal degradation of "FeS₄C₄Ph₄" affords a sulfur-bridged dimeric complex of composition Fe₂S₂(S₂C₂Ph₂)₂. The same compound is also formed from the reaction of metallic iron or iron carbonyls with sulfur and diphenylacetylene under conditions similar to the original preparation of NiS₄C₄Ph₄. Both "FeS₄C₄Ph₄" and "CoS₄C₄Ph₄" form stable five-coordinate 1:1 adducts with phosphines. A well-defined tributylphosphine adduct of FeS₄C₄H₄ is also reported. The phosphine adducts of the iron complexes may be regarded as isoelectronic with the neutral nickel compounds NiS₄C₄R₄, and the analogous compounds of cobalt as isoelectronic with NiS₄C₄R₄⁻. The reaction of the Fe, Co, and Ni complexes MS₄C₄R₄ with Fe(CO)₅ affords the compounds Fe₂(CO)₆C₂S₂R₂, of which several derivatives, including Fe₂(CO)₆S₂C₂H₂, are also described. The bonding in the complexes is discussed and additional evidence in support of the proposed delocalized ground states of the compounds is presented.

In the course of our work on dithiodiketone complexes of transition metals, the bisdithiobenzil complexes of iron and cobalt so far have been men-

(1) (a) Paper XI of the series: The Chemistry of Coordination Compounds. (b) Paper X: G. N. Schrauzer, and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 3235 (1966).

(2) Department of Chemistry, The University of California at San Diego, La Jolla, Calif.

tioned only briefly.³ Neutral complexes of iron and cobalt were reported by Davison, *et al.*,⁴ with S₂C₂-(CF₃)₂ as ligands. The iron compound was initially

(3) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 381 (1964).

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