Table IV. Analytical and Infrared Spectral Data for $Cr(CO)_5L$

L	% C		% H		ν_{CO}, cm^{-1}
	Calcd	Found	Calcd	Found	
$(C_2H_5)_3P$[a]	42.58	42.77	4.88	5.15	1935 s, 1945 m, 2055 w
$(C_2H_3)_3P$	43.43	43.40	2.99	2.78	1930 m, 1950 s, 2070 m
$(C_2H_5)_2S$[b]					1935 m, 1945 s, 1985 w, 2060 w
$(CH_3)_2S$[c]					1935 m, 1945 s, 1990 w, 2065 w
$(CH_3)(CH_2Cl)S$	29.13	29.43	1.75	1.80	1945 s,[d] 2065 w
$(C_2H_3)_2S$					1935 m, 1945 s, 2065 w

[a] See ref 14 for reported ν_{CO} values. [b] See ref 15 for characterization of this complex. [c] See ref 16 for characterization of this complex. [d] Second peak in this region not resolved.

The b_1 orbital, essentially nonbonding, has a measured IP of 8.69 eV (Table II), while the a_1 orbital, with more bonding character than the b_1 but still highly localized on sulfur, has a measured IP of 11.20 eV. As the acid is moved closer to the ligand, the two highest occupied molecular orbitals retain essentially the configuration found for the free base, taking on acid character as the acid–base distance is lowered and tilting slightly as the distance approaches 2.0 Å. Thus it may be assumed that IP_3 and IP_4 (if measurable) in the sulfide complexes can be correlated in order with the two highest occupied molecular orbitals of the free sulfide bases, with the addition of some Cr bonding character. In the phosphine complexes, IP_3 is correlated with the lone-pair orbital (a_1) of the uncomplexed R_3P and is considered to involve Cr σ bonding.[2] On the basis of these assignments, stabilization energies are obtained for the appropriate ligand orbitals upon complexation. They are given in Table III, using the orbital designation for the uncomplexed species. The b_1 orbital is stablized by ca. 50% more than the a_1 orbital in those sulfide complexes where both IP's are measured. This is qualitatively consistent with the sample calculation, which showed the b_1 orbital stabilized by ca. twice as much as the a_1 orbital with the approach of the Lewis acid. Since the stabilization energies reflect the degree to which complexation perturbs the highest occupied ligand orbitals, the variation in stabilization energies with the changing substituent R reflects the influence of R on the ligating properties of the donor. Thus the presence of electron-donating alkyl groups results in a greater perturbation of the ligand orbitals upon complexation than with the more electron-withdrawing substituents. This appears so despite the varying structural and conjugative factors which may influence the energies of the lone-pair orbitals of the uncomplexed ligands.

Experimental Section

Preparation of Compounds. The complexes were prepared by the method of Connor[10] from the salt $[Et_4N^+][Cr(CO)_5Br^-]$, ca. 10–20% molar excess of the phosphine or sulfide, and $Et_3O^+BF_4^-$ in methylene chloride solution at room temperature. The halide starting material was prepared by the method of Abel.[11] The complexes were purified by sublimation onto a cold finger and chilled with dry ice–acetone. The Et_3P and Me_2S complexes were obtained as low-melting solids, mp 25–29 and 11–14 °C, respectively, while the others were obtained as oils.

The complexes could be easily and clearly characterized by their mass spectra, since the initial fragmentation is dominated by peak clusters corresponding to the successive loss of CO groups.[12] Peaks of mass number greater than the molecular ion could be assigned to $M(CO)_4L_2^+$, and the presence of $M(CO)_6^+$ could easily be detected. Traces of disubstituted product were found in the spectra of the phosphine complexes, while $Cr(CO)_6$ was found in the spectra of the divinyl sulfide and $(CH_3)(CH_2Cl)S$ derivatives.

Table IV lists the analytical data for the new complexes prepared (except for the divinyl sulfide complex), as well as the values of ν_{CO}. The infrared spectra were obtained on hexane solutions, using a Perkin-Elmer Model 247 spectrophotometer. An extra peak at 1980 cm^{-1} in the vinyl and chloromethyl derivatives indicated the presence of $Cr(CO)_6$.[13] A weak band at ca. 1910 cm^{-1} in many of the spectra is of unknown origin.

Measurement of Photoelectron Spectra. The spectra were obtained with a Perkin-Elmer Model PS-18 spectrometer, using the He I resonance line (21.22 eV). Since elevated temperatures were necessary for proper vapor pressures of the complexes investigated, a direct-inlet probe was used. The spectra were calibrated with Ar (15.76-eV line) and Xe (12.13-eV line) as internal standards. The IP values listed are the band maxima.

Registry No. $Cr(CO)_5(C_2H_5)_3P$, 21321-30-2; $Cr(CO)_5(C_2H_3)_3P$, 65338-52-5; $Cr(CO)_5(C_2H_5)_2S$, 60149-92-0; $Cr(CO)_5(CH_3)_2S$, 31172-83-5; $Cr(CO)_5(CH_3)(CH_2Cl)S$, 65338-63-8; $Cr(CO)_5(C_2H_3)_2S$, 65338-62-7; $(C_2H_5)_3P$, 554-70-1; $(C_2H_3)_3P$, 3746-01-8; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; $(C_2H_3)_2S$, 627-51-0; $(CH_3)(CH_2Cl)S$, 2373-51-5.

Supplementary Material Available: Figure showing the photoelectron spectra of the complexes (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) R. F. Fenske, *Prog. Inorg. Chem.*, **21**, 179 (1976).
(2) B. R. Higginson, D. R. Lloyd, J. A. Connor and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1418 (1974).
(3) B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1659 (1973).
(4) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).
(5) E. W. Ainscough, E. J. Birch, and A. M. Brodie, *Inorg. Chim. Acta*, **20**, 187 (1976).
(6) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
(7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(8) G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974). See also D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.*, **76**, 1030 (1972).
(9) K. A. Ostoja-Starzewski, H. Tom-Dieck, and H. Bock, *J. Am. Chem. Soc.*, **98**, 8486 (1976).
(10) J. A. Connor, E. M. Jones, and G. K. McEwen, *J. Organomet. Chem.*, **43**, 357 (1972).
(11) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
(12) J. Miller, *Angew. Chem., Int. Ed. Engl.*, **11**, 653 (1972).
(13) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).
(14) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc. A*, 1195 (1968).
(15) H. G. Raubenheimer, J. C. A. Boeyens, and S. Lotz, *J. Organomet. Chem.*, **112**, 145 (1976).
(16) W. Ehrl and H. Varenkamp, *Chem. Ber.*, **103**, 3563 (1970).

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Preparation of Dithiocarbamate Ligands Derived from Indole, Indoline, Carbazole, and Imidazole and Representative Transition-Element Complexes

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We recently reported the preparation of the pyrrolecarbodithioate ligand and selected transition-element complexes[1] exploiting a route first outlined by Trofimenko in the preparation of the 1-pyrazolecarbodithioate ligand.[2] This synthetic scheme seems to offer potential for a general route to new ligand systems, especially for those dithiocarbamates derived from less basic amines.

For some time, it has generally been accepted that dithiocarbamates derived from indole, indoline, carbazole, and imidazole were nonexistent, although theoretical treatises proposing the relative properties of some of these may be found.[3] The major failure of these amines to form dithiocarbamates has been the inability of the usual synthetic routes to sufficiently activate the amine proton.[4] In an effort, then, to ascertain not only the range of applicability of this synthetic method mentioned above but also to investigate the behavior exhibited by these dithiocarbamates and their complexes, we have extended our previous work to the title complexes.

In this study, we were particularly interested in gaining some information on the predominant resonance forms of dithiocarbamates and their contribution to the ligand field strengths of these ligands.

Experimental Section

Materials. Reagent grade acetonitrile was dried by repeated distillation from phosphorus pentoxide. Tetrahydrofuran and hexanes were dried over Na/K alloy and benzophenone. Carbon disulfide, chloroform, and pyridine were dried over Davison 4-Å molecular sieves. $CuBr_2$, $ZnBr_2$, $CdBr_2$, $NiBr_2$, and $FeBr_3$ were obtained from Research Organic/Inorganic, Inc. $CuCl_2{\cdot}2H_2O$, $FeCl_3$, $CdCl_2{\cdot}2.5H_2O$, $NiCl_2{\cdot}6H_2O$, and $ZnCl_2$ were obtained from Fisher Scientific Co.

Preparation of Compounds. (A) Preparation of the Dithiocarbamates of Indole, Indoline, Carbazole, and Imidazole. To 0.050 mol of the parent amine dissolved in 100 mL of dry tetrahydrofuran was added 1.95 g (0.050 mol) of potassium metal. After the reaction was allowed to proceed for 24 h, the mixture was cooled to −78 °C and 3.9 g (3.1 mL, 0.060 mol) of carbon disulfide was added dropwise over a 0.5-h period. The resulting red-yellow solutions were stirred for an additional hour. After this period, chilled (−20 °C), degassed hexanes were added causing the product to precipitate.[5] This precipitate was isolated by filtration in high yield and purity. In this manner the following compounds were prepared.

(1) The bright yellow potassium indolinecarbodithioate was obtained in >90% yield (mp 240 °C dec). The complex is relatively air stable. Anal. Calcd for $C_9H_8S_2NK{\cdot}C_4H_8O$: C, 51.11; H, 5.28; N, 4.58; S, 20.99. Found: C, 51.27; H, 5.30; N, 4.45; S, 20.79.

(2) The bright yellow, highly hygroscopic potassium indolecarbodithioate was obtained in 90% yield (mp 58–61 °C). The compound is extremely air sensitive, decomposing in a matter of minutes into a dark brown oil. Anal. Calcd for $C_9H_6S_2NK{\cdot}C_4H_8O$: C, 51.45; H, 4.65; N, 4.62; S, 21.13. Found: C, 51.59; H, 4.52; N, 4.79; S, 21.24.

(3) The bright yellow-orange, highly hygroscopic potassium carbazolecarbodithioate was obtained in 80% yield (mp 120 °C dec). The compound is extremely air sensitive, decomposing in 30 s into a black tar. Anal. Calcd for $C_{13}H_8S_2NK{\cdot}C_4H_8O$: C, 57.75; H, 4.56; N, 3.96; S, 18.14. Found: C, 57.57; H, 4.50; N, 4.02; S, 17.90.

(4) The pale yellow potassium imidazolecarbodithioate was obtained in 90% yield (mp 158–161 °C). The complex is relatively air stable. Anal. Calcd for $C_4H_3N_2S_2K{\cdot}{}^1/_2C_3H_3N_2$: C, 30.60; H, 2.10; N, 19.46. Found: C, 30.95; H, 2.29; N, 19.72.

(B) Preparation of the Transition-Metal Complexes [M = Cu(II), Ni(II), Cd(II), Zn(II), Fe(III)]. Two general synthetic routes were employed to generate these analogues: (1) For those dithiocarbamate salts which were air stable, reactions were carried out in 50/50 H_2O/ethanol mixtures. (2) For those dithiocarbamate salts which were air sensitive, reactions were carried out in dry acetonitrile. A detailed description of each synthetic route is given below.

Method 1: Preparation of Transition-Metal Complexes of Indolinecarbodithioate and Imidazolecarbodithioate. To 0.0040 mol of the corresponding dithiocarbamate dissolved in 50 mL of ethanol was added dropwise 0.0020 mol of the corresponding metal chloride dissolved in 50 mL of H_2O. The resulting metal complexes precipitated from solution, and after being stirred for an additional hour, the mixture was filtered and the precipitate was washed consecutively with five 20-mL portions of water and five 20-mL portions of 95% ethanol and then dried under vacuum. Samples of high purity were obtained directly.

Table I

Compd	Color	Compd	Color
L = Indolinecarbodithioate			
$C_{18}H_{16}N_2S_4Cu$	Brown	$C_{18}H_{16}N_2S_4Cd$	White
$C_{18}H_{16}N_2S_4Ni$	Orange-yellow	$C_{27}H_{24}N_3S_6Fe$	Red
$C_{18}H_{16}N_2Zn$	White		
L = Indolecarbodithioate			
$C_{18}H_{12}N_2S_4Cu$	Brown	$C_{18}H_{12}N_2S_4Cd$	Orange-yellow
$C_{18}H_{12}N_2S_4Ni$	Red	$C_{27}H_{18}N_3S_6Fe$	Reddish purple
$C_{18}H_{12}N_2S_4Zn$	Orange-yellow		
L = Imidazolecarbodithioate			
$C_8H_6N_4S_4Cu$	Brown	$C_8H_6N_4S_4Zn$	White
$C_8H_6N_4S_4Ni$	Brownish-green	$C_8H_6N_4S_4Cd$	White
L = Carbazolecarbodithioate			
$C_{26}H_{16}N_2S_4Cu$	Brown	$C_{26}H_{16}S_4Cd$	Pale yellow
$C_{26}H_{16}N_2S_4Ni$	Dark red	$C_{39}H_{24}N_3S_6Fe$	Reddish purple
$C_{26}H_{16}N_2S_4Zn$	Pale yellow		

Method 2: Preparation of Transition-Metal Complexes of Indolecarbodithioate and Carbazolecarbodithioate. To 0.0080 mol of the corresponding dithiocarbamate dissolved in 200 mL of dry acetonitrile was added 0.0040 mol of the appropriate metal bromide.

After being stirred for 5 h, the reaction mixture was filtered to remove KBr (and some of the metal complex which also precipitated). The filtrate was reduced to half its original volume and refrigerated for 24 h. A fine-powdered precipitate of the corresponding complexes formed and was collected by filtration. Further crops of the complexes could be obtained by successive volume reduction. The Cu(II), Zn(II), Cd(II), and Ni(II) complexes for indoline-, indole-, imidazole-, and carbazolecarbodithioates were prepared. Only the indoline-, indole-, and carbazolecarbodithioate ligands gave Fe(III) complexes. The color and listing of these complexes is given in Table I. Acceptable elemental analyses were obtained on all of the complexes reported.

Analyses. Analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn., and the microanalytic laboratory of this department.

Methods. The preparation of the parent potassium salts were carried out under an argon atmosphere using Schlenk techniques. Similar manipulations were employed for the preparation of the transition-metal complexes of the indole and carbazole derivatives. NMR and melting point tubes were sealed under vacuum in the case of potassium indole and carbazole derivatives.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at 17 °C using the Gouy method. Pascal's constants were used to correct the measurements for diamagnetic contributions of the ligand and core electrons of the metal.[6]

Spectroscopic Measurements. Infrared spectra were obtained as Nujol mulls and KBr pellets on a Perkin-Elmer Model 467 spectrophotometer. Optical spectra were obtained as Nujol mulls (diffuse absorption), in CH_3Cl and in 60/40 CH_3Cl/pyridine solutions, on a Cary Model 14 spectrophotometer. Electron spin resonance spectra were obtained at 9.0 GHz employing a Varian E-9 spectrometer coupled to a Hewlett-Packard Frequency Meter and DPPH as a *g*-value standard. All ESR spectra were obtained at 100 K as previously described.[1] Nuclear magnetic resonance spectra were obtained on a Varian XL-100 Fourier transform spectrometer.

Results and Discussion

Each of these dithiocarbamates represents, to the best of our knowledge, the first successful isolation of these individual species. These results demonstrate the overall applicability of the synthetic route to dithiocarbamate ligands, especially in light of the report that earlier attempts to prepare these carbamates were unsuccessful.[4]

Resonance forms of the type depicted in **1B** have been shown

1A 1B

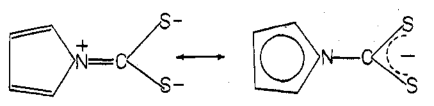
to play an important role in influencing the overall structure and properties of most all other dithiocarbamate systems

Table II. ESR Parameters

Compd	$A_\parallel$[a]	$A_\perp$[a]	$g_\parallel$	$g_\perp$	$\langle a\rangle$[a]	$\langle g\rangle$	α	β	δ
Copper indolinecarbodithioate	144.4	31.5	2.11	2.026	62.4	2.078	0.73	0.79	0.77
Copper indolecarbodithioate	139.0	23.2	2.12	2.029	57.8	2.058	0.72	0.80	0.80
Copper carbazolecarbodithioate	141.6	23.5	2.11	2.026	58.9	2.068	0.72	0.81	0.78

[a] Values are listed as $\text{cm}^{-1} \times 10^4$.

previously studied.[7-10] Yet, in our characterization of the pyrrole system, we have shown that by an appropriate choice of amines, a dithiocarbamate exhibiting rather unusual properties due to a major contribution of the resonance structure depicted in **2B** could be prepared. Since there is an equally strong criterion for this phenomenon in all of these new species as well, one would then expect that a predominance of resonance forms of the type depicted in **1B** or **2A** to be of little or no significance in influencing the overall chemical or physical properties of these dithiocarbamates when complexed to a metal. In order to test this premise, a series of representative complexes were characterized.



2A 2B

The important IR, NMR, and optical features of these metal complexes as well as suggested assignments are available as supplementary material. The complex NMR spectra prevent a detailed evaluation of the electron-density distribution in the ring systems as has been possible before.[1] We do observe a relatively large shift downfield for the 2 and 7 protons in indole to 9.05 and 8.4 ppm in the diamagnetic transition-metal complexes and a corresponding shift of the 7 proton in indoline to 8.7 ppm in its complexes. Subsequent shifts of the 2 and 5 protons in carbazole are observed at 7.7 and 8.7 ppm, respectively. Sebastian et al., however, have shown that these proton shifts (specifically for indole) do not necessarily reflect a change in electron density.[11] A rough estimate of the J_{23} coupling constants could be obtained in certain cases and in each case were nearly equal to those of the parent amine, suggesting that very little perturbation of the electron density in the ring has occurred as the dithiocarbamate is formed or as complexation is taking place.

For the Cu(II) complexes, a more sensitive probe exists to explore the local electron density at the metal center. Table II lists the spin Hamiltonian parameters for the copper complexes in 60/40 $CHCl_3$/pyridine.[12]

On the basis of these data, it can be assumed that the local symmetry about the copper atom involves an effective C_4 symmetry. As such, one can readily observe the relative electronic distribution by calculating the bonding parameters with the usual procedures[13-15] and modified set of equations previously employed.[16]

$$g_\parallel' = 2.0023 - (8\lambda/\Delta E_{xy})\alpha^2\beta^2 \tag{1}$$

$$g_\perp = 2.0023 - (2\lambda/\Delta E_{xz})\alpha^2\delta^2 \tag{2}$$

$$A_\parallel = P\alpha^2 \left\{ -\left(\frac{4}{7} + k\right) - 2\lambda\left[\frac{4\beta^2}{\Delta E_{xz}} + \frac{3}{7}\left(\frac{\delta^2}{\Delta E_{xz}}\right)\right]\right\} \tag{3}$$

The calculated values for α, β, and δ (the coefficient for the *d portion* of the appropriate molecular orbital) appearing in Table II indicate a strong covalency in the in-plane σ bonding and moderate covalency for the in-plane and out-of-plane π bonding. Of particular interest is the value of the out-of-plane π bonding since we have previously observed that trends in this value indicate the relative importance or, in fact, the predominance of a particular resonance form in influencing the overall properties of a complex.[1,16] Therefore, to properly describe the overall bonding one must suggest a bonding scheme where multiple M–S bond character arises as the result of the interaction of filled d orbitals on the metal with empty ligand π orbitals arising from the sulfur atoms.

Further support to confirm this particular mode of bonding is readily accessible from magnetic susceptibility studies. Increasing the effective π bonding will result in a shorter M–S bond and thus a larger Δ, which favors the low-spin state. Numerous other reports correlating high spin–low spin states to magnetic susceptibilities in terms of structural comparison,[17-19] NMR studies,[19] and IR[20] data serve to confirm these postulates. We have observed solid-state magnetic moments for the iron complexes of the dithiocarbamates of indoline, indole, and carbazole to be 2.40, 2.45, and 2.53 μ_B, respectively. The ESR observations and to a lesser extent the IR and NMR data suggest that these dithiocarbamate complexes exhibit a predominance of resonance form **2B** and it is this which is the *strong-field* form for dithiocarbamates.

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Registry No. Copper indolinecarbodithioate, 65495-62-7; nickel indolinecarbodithioate, 65495-61-6; zinc indolinecarbodithioate, 65495-60-5; cadmium indolinecarbodithioate, 65516-33-8; iron indolinecarbodithioate, 40214-99-1; copper indolecarbodithioate, 65495-59-2; nickel indolecarbodithioate, 65495-58-1; zinc indolecarbodithioate, 65495-57-0; cadmium indolecarbodithioate, 65495-56-9; iron indolecarbodithioate, 65495-55-8; copper imidazolecarbodithioate, 65495-54-7; nickel imidazolecarbodithioate, 65495-53-6; zinc imidazolecarbodithioate, 65495-52-5; cadmium imidazolecarbodithioate, 65495-51-4; copper carbazolecarbodithioate, 65495-50-3; nickel carbazolecarbodithioate, 65495-49-0; zinc carbazolecarbodithioate, 65495-48-9; cadmium carbazolecarbodithioate, 65495-47-8; iron carbazolecarbodithioate, 65495-46-7; potassium indolinecarbodithioate, 65484-15-3; potassium indolecarbodithioate, 65484-14-2; potassium carbazolecarbodithioate, 55720-50-8; potassium imidazolecarbodithioate, 65484-13-1; indole, 120-72-9; indoline, 496-15-1; carbazole, 86-74-8; imidazole, 288-32-4; carbon disulfide, 75-15-0.

Supplementary Material Available: Tables of analytical results as well as infrared and optical data (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. D. Bereman and D. Nalewajek, *Inorg. Chem.*, **16** 2687 (1977).
(2) S. Trofimenko, *J. Org. Chem.*, **33**, 890 (1968).
(3) R. Eley and N. Duffy, *J. Inorg. Nucl. Chem.*, **34**, 3681 (1972).
(4) R. Eley, R. Myers and N. Duffy, *Inorg. Chem.*, **11**, 1128 (1972).
(5) Potassium indolinecarbodithioate readily precipitates out of the tetrahydrofuran solution without the addition of hexanes.
(6) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960, p 403.
(7) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 294 (1970).
(8) J. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(9) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
(10) G. Thorn, R. Ludwig, "Dithiocarbamates and Related Compounds", American Elseivier, New York, N.Y., 1962.
(11) J. Sebastian, M. Reinecke, H. Johnson, Jr., *J. Phys. Chem.*, **73**, 455 (1969).
(12) Similar values for these parameters were obtained in 50/50 DMF/$CHCl_3$ solutions. Overall, we observed an increase of ~4–5 G for $A_\parallel$, 2–3 G for $A_\perp$, and a net change of ±0.1 for $g_\parallel$ and $g_\perp$.
(13) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).
(14) H. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).
(15) R. Nieman and D. Kivelson, *J. Chem. Phys.*, **35**, 149, 156, 162 (1961).
(16) R. Bereman and P. Savino, *Inorg. Chem.*, **12**, 173 (1973).
(17) P. Healy and A. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
(18) P. Healy and A. White, *Chem. Commun.*, 1446 (1971).
(19) R. Golding and W. Tennant, *J. Chem. Phys.*, **45**, 2688 (1966).
(20) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).