state of the molecule. The excited states of both the ligand $n \rightarrow \pi^*$ transition and the $M(LH_2)_2X_2$ $M(d) \rightarrow L\ \pi^*$ transitions are derived from the lowest unoccupied π^* orbital of the ligand. Therefore, the bonding interactions and percent character composition for the two excited states are qualitatively very similar.

This interpretation of the spectrum allows several observations to be explained. The initial weak band at 704 nm is a $M(d) \rightarrow L\ \pi^*$ transition rather than a $d \rightarrow d$ transition as previously advanced but exhibits a weak coupling to a vibrational mode resulting in a low intensity. The loss of this band in the solution spectrum (Figure 3a) can be explained with the assumption, in analogy to the free ligand, that this band gains most of its intensity by coupling to a lattice mode that would not exist in the solution spectrum. In addition, it has been reported[21c] that in the solid-state KBr spectra for the $M(N,N'\text{-}Me_2dto)_2Br_2$ complexes (M = Ni, Pd, Pt) the relative intensities and energetic spacings of the absorption bands in the visible region were scarcely influenced by the central metal. This observation can be explained quite readily according to our interpretation of the spectral data, which states that the relative intensities and energetic spacings of these bands would not be dependent on the central metal but rather on the energy of the coupled vibrational frequencies and on the intensity pattern of their associated Franck–Condon progressions.

Summary

In agreement with the previous spectral assignment of dithiooxamides,[20] the UV–vis spectrum for dithiooxamide has been shown to consist of two bands. The first band is a weak broad $n \rightarrow \pi^*$ transition occurring in the visible region and is assigned as ${}^1A_u \leftarrow {}^1A_g$ ($13a_g \rightarrow 4a_u$). The second band is an intense broad $\pi \rightarrow \pi^*$ transition occurring in the UV region and is assigned as ${}^1B_u \leftarrow {}^1A_g$ ($3b_g \rightarrow 4a_u$). Symmetrical N,N′-dialkylation of the dto moiety has been shown to cause a blue shift and an increase in the molar absorptivity value for both of the transitions. A red shift of the transitions was observed for *N,N′*-bis(trimethylsilyl)dithiooxamide.

The $n \rightarrow \pi^*$ transition of the dithiooxamides reported here exhibits heretofore unreported vibrational fine structure, which clearly resolves upon temperature reduction. A preliminary analysis of the spectral data of $N,N'\text{-}Bzl_2dto$ indicates that at least three vibrational frequencies are contributing to the observed spectrum. The two lower energy frequencies of ca. 52 and ca. 180 cm^{-1} are tentatively assigned as crystal lattice modes, while the major vibrational progression with a frequency of ca. 1150 cm^{-1} appears to involve the C–C stretch.

The spectra for $Ni(N,N'\text{-}Bzl_2dto)_2Br_2$, which is representative of the $M(LH_2)_2X_2$ complexes, have been shown to consist of a series of bands in the visible region of varying intensity and an intense broad band in the UV region. In contrast to the previous assignment,[21c] the UV band is assigned as a $L\ \pi \rightarrow L\ \pi^*$ transition. In partial agreement with the previous assignments,[21a,c] the bands in the visible region for the $M(LH_2)_2X_2$ complexes are assigned as $M(d) \rightarrow L\ \pi^*$ transitions. However, the weak low-energy bands are not $d \rightarrow d$ transitions as previously advanced but are $M(d) \rightarrow \pi^*$ transitions. The multiplicity of bands in the visible region is caused by the coupling of one or more vibrational modes to allowed $M(d) \rightarrow L\ \pi^*$ transitions. The major vibrational progression resolves upon temperature reduction and appears to be qualitatively very similar to the major vibrational progression observed for the $n \rightarrow \pi^*$ transition of the free ligand.

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Notes

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Intervalence Transfer in the Dimer $[(NH_3)_5Ru^{II}(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{5+}$

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In the study of mixed-valence compounds, ligand-bridged dimers based on the $[(NH_3)_5Ru^{III/II}]$ couple have played a central role.[1] Notable examples include the Creutz and Taube ion,[2] $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ (pz = pyrazine), where the question of localization vs. delocalization is a source of continuing debate,[1-3] and the analogous 4,4′-bipyridine-bridged dimer, $[(NH_3)_5Ru^{II}(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{5+}$, where the valences appear to be trapped and the properties are well-defined in terms of available theory.[4]

We have reinvestigated a particular property of the latter ion, the solvent dependence of the energy of its intervalence transfer (IT) or metal–metal charge-transfer (MMCT) absorption band. On the basis of the results of our study and in light of recent developments in the area, we conclude that (1) there is a considerable contribution to the apparent IT band energy arising from the existence of multiple IT transitions, (2) application of dielectric continuum theory to the solvent dependence of the IT band energy is not quantitatively successful, and (3) solvent effects whose origins arise at the molecular level may play a role in dictating the observed absorption band energies.

According to Hush,[5] the band energy (E_{op}) for intervalence transfer in a chemically symmetrical mixed-valence dimer where electronic coupling is energetically negligible is given by

$$E_{op} = \chi_i + \chi_s \qquad (1)$$

where χ_i and χ_s are the intramolecular (inner coordination sphere) and solvent reorganization or trapping energies, respectively. From dielectric continuum theory, χ_s is given by[5]

$$\chi_s = e^2\left(\frac{1}{r} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (2)$$

In eq 2, e is the unit electronic charge, r is the molecular radius of the redox sites, d is the separation distance between trapping sites, and D_{op} and D_s are the optical and static dielectric constants of the solvent. The result in eq 2 is based on the assumption that the redox sites can be treated as nonpenetrating spheres. The effect of solvent has also been treated on the basis of the electronic redistribution that occurs within an ellipse enclosing the ion.[6] For the case of interest here, the two-sphere model would appear to

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(1) See, for example: (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Taube, H. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 481.

(2) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086.

(3) Fuerholz, U.; Bürgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.

(4) (a) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7828. (b) Creutz, C. *Inorg. Chem.* **1978**, *17*, 3723.

(5) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(6) (a) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657. (b) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299. (c) Kharkats, Yu I. *Electrokhimya* **1976**, *15*, 1251. (d) German, E. D. *Chem. Phys. Lett.* **1979**, *64*, 305.

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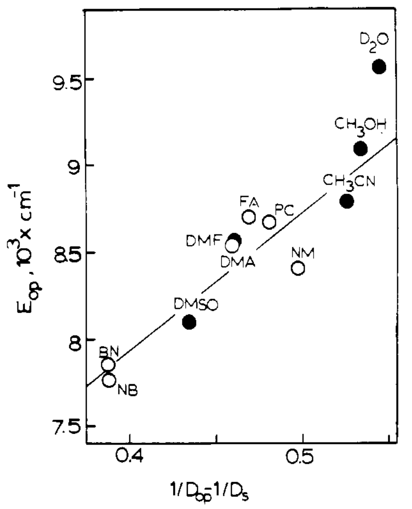
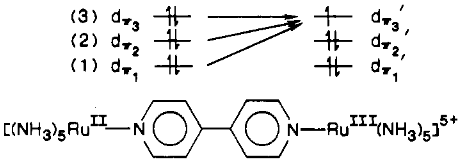


Figure 1. Intervalence transfer band energies vs. $(1/D_{op} - 1/D_s)$: (○) this work; (●) ref 4. Key to solvents: BN = benzonitrile, NB = nitrobenzene, DMSO = dimethyl sulfoxide, DMF = dimethylformamide, DMA = dimethylacetamide, PC = propylene carbonate, FA = formamide, NM = nitromethane.

Scheme I



be as appropriate as the ellipsoidal cavity model and the results have the advantage of being physically more transparent for the two-sphere model.

In Figure 1 is shown a plot of the IT transition energy (E_{op}) vs. $(1/D_{op} - 1/D_s)$[7] for the transition

$$[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+} \xrightarrow{h\nu} [(NH_3)_5Ru^{III}(4,4'\text{-bpy})Ru^{II}(NH_3)_5]^{5+} \quad (3)$$

From the plot, a linear correlation exists although the point for D_2O is three standard deviations (σ = 170 cm^{-1}) above the best-fit line for the remaining solvent. Omitting D_2O[8] gives an intercept of 4820 cm^{-1} and slope of 7810 cm^{-1}, which differ substantially from those reported earlier (intercept = 2500 cm^{-1}; slope = 13 500 cm^{-1}), which were based on fewer solvents and included D_2O.[4b]

From eq 1 and 2 the intercept of the plot is predicted to equal χ_i. From bond length data for $[(NH_3)_5Ru(pz)]^{2+}$ and $[(NH_3)_5Ru(pz)]^{3+}$ (pz is pyrazine),[9] Creutz has calculated $\chi_i \approx$ 1400 cm^{-1},[4b] giving a calculated intercept that is far less than that estimated by using the data presented here. In retrospect, the discrepancy is expected when a more detailed analysis is applied to the IT "band".[6a,10,11] In symmetries lower than O_h, including spin-orbit coupling, the three d_π orbitals, which are initially t_{2g} and degenerate in O_h symmetry, are split into d_{π_1}, d_{π_2}, and d_{π_3}. As shown in Scheme I the lifting of the degeneracy in the d_π levels leads to three possible IT transitions. The energies of the corresponding IT absorption bands are predicted to be separated approximately by the energies of the Ru^{III}-based inter d_π' (spin-orbit) states $E_{d_\pi}(2)$ and $E_{d_\pi}(1)$ as[10]

$$E_{IT}(1)(d_{\pi_3} \rightarrow d_{\pi_3}') \quad (4)$$

$$E_{IT}(2)(d_{\pi_2} \rightarrow d_{\pi_3}') = E_{IT}(1) + E_{d_\pi}(1) \quad (5)$$

$$E_{IT}(3)(d_{\pi_1} \rightarrow d_{\pi_3}') = E_{IT}(1) + E_{d_\pi}(2) \quad (6)$$

In fact, multiple IT transitions are observed for mixed-valence osmium dimers[10,14] where the spin-orbit coupling constant is large ($\lambda_{Os} \sim$ 3000 cm^{-1}). Excited-state IT transitions ($d_\pi^{Fe} \rightarrow d_\sigma^*{}_{Fe}$) have also been reported in cyanoiron mixed-valence solids.[12] For Ru, where the spin-orbit coupling is lower ($\lambda_{Ru} \sim$ 1100 cm^{-1}), the three IT bands are, in general, not resolvable. However, of the three IT components the two arising from a linear combination of d_{xz} and d_{yz} (defining the z axis as lying along the Ru(4,4'-bpy)Ru axis) should be the most allowed, because of extensive mixing with π^*(4,4'-bpy) levels, and these should provide the majority of the intensity to the IT manifold. Stabilization of d_{π_1} and d_{π_2} by mixing with π^*(4,4'-bpy) also means that the transitions $d_{\pi_1} \rightarrow d_{\pi_3}'$ and $d_{\pi_2} \rightarrow d_{\pi_3}'$ will occur on the high-energy side of the IT manifold.

The analysis outlined above provides a qualitative basis for understanding the large intercept obtained in the solvent dependence plot. Equation 1 is only applicable to the lowest of the three IT transitions. The actual IT band energy will include contributions from all three components at energies $E_{IT}(1)$, $E_{IT}(1) + E_{d_\pi}(1)$, and $E_{IT}(1) + E_{d_\pi}(2)$ with the intensity distribution skewed toward the higher energy components. E_{op} is related to $E_{IT}(1)$ by the relationship $E_{op} \sim E_{IT}(1) + \Delta$, where Δ is the energy difference between the absorption band maximum arising from the higher energy components and $E_{IT}(1)$ (eq 7).

$$E_{op} = \chi_i + \chi_o + \Delta \quad (7)$$

In the related Os(III)–Os(III) dimer $[(NH_3)_5Os(4,4'\text{-bpy})Os(NH_3)_5]^{6+}$, inter d_π transitions are observed at $E_{d_\pi}(1) \sim$ 4800 and $E_{d_\pi}(2) \sim$ 5600 cm^{-1}.[13] Since $\lambda_{Ru} \sim$ 1100 cm^{-1} and $\lambda_{Os} \sim$ 3000 cm^{-1}, $E_{d_\pi}(1)$ and $E_{d_\pi}(2)$ for the Ru dimer are predicted to occur at approximately 1800 and 2100 cm^{-1}.[14] Taking an average value of 1900 cm^{-1} and assuming that the intensity of the IT manifold is dominated by the d_{π_1},d_{π_2}-based transitions gives $\Delta \sim$ 1900 cm^{-1}. Since the intercept should equal the sum of χ_i and Δ, a Δ value of this magnitude would help to account for the large intercept in the solvent dependence experiment.

From eq 2 and dielectric continuum theory it is possible to calculate the slope of the E_{op} vs. $(1/D_{op} - 1/D_s)$ plot in Figure 1. Using r = 3.5 Å and d = 11.3 Å gives $\delta E_{op}/\delta(1/D_{op} - 1/D_s)$ = 22 500 cm^{-1}, which is only 35% of the experimental value. The disagreement is particularly striking in view of the nearly quantitative agreement with dielectric continuum theory found for the dimer $[(bpy)_2ClRu^{III}(4,4'\text{-bpy})Ru^{II}Cl(bpy)_2]^{3+}$.[15] The lower than expected sensitivity to solvent for the pentaamine-based dimer has also been observed by treating the earlier, somewhat limited solvent dependence data by using the ellipsoidal cavity model.[6a] It was suggested there that the origin of the effect may lie in specific interactions with coordinated NH_3, which would tend to restrict the motion of nearest neighbor solvent molecules, which would be manifested as a local saturation of the solvent dielectric.

At the very least, the discrepancy shows that dielectric continuum theory does not provide a satisfactory quantitative basis for understanding the role of solvent in the IT transition for the decaammine dimer. There are some additional implications of the result that are notable. (1) In contrast to the optical experiment, the solvent contribution to thermal self-exchange for reactions like $[(NH_3)_5Ru(py)]^{3+/2+}$ appears to be well described by dielectric continuum theory.[16] It is difficult to imagine that

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(7) E_{op} values were obtained from near-IR spectra by using a Cary 17 spectrometer. The preparation of $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5](PF_6)_4$ is described in ref 4. The mixed-valence form was obtained in situ by using Br_2 vapor as oxidant or by preparing the fully oxidized PF_6^-,Br^- mixed salt in solid form and combining it with an equimolar quantity of the fully reduced complex.

(8) Including D_2O: slope = 9010 cm^{-1}; intercept = 4300 cm^{-1}.

(9) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522.

(10) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *105*, 4303.

(11) (a) Goldsby, K. A. Ph.D. Thesis, The University of North Carolina, 1983. (b) Kober, E. M. Ph.D. Thesis, The University of North Carolina, 1982.

(12) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(13) Magnuson, R. H.; Lay, P. A.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 2507.

(14) A more exact analysis would calculate $E_{d_\pi}(1)$ and $E_{d_\pi}(2)$ as the sum of distinct contributions from spin-orbit coupling and ligand field asymmetry.

(15) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

(16) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

the theory would be adequate for one problem and not the other, and perhaps additional ingredients exist in the self-exchange kinetics that lead to a fortuitous agreement or perhaps a simple relationship between optical and thermal electron transfer does not exist for ammine complexes. (2) One criterion that has been cited in support of a delocalized description for the dimer $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ is the absence of a significant solvent dependence.[1] However, given the relatively slight dependence of E_{op} on solvent in the 4,4′-bpy dimer, noting that in the related, valence-trapped system $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$ the substitution of L = 4,4′-bpy by L = pyrazine decreases $\delta E_{op}/\delta(1/D_{op} - 1/D_s)$ by twofold, the solvent dependence criterion for delocalization may not be fully valid. (3) From the results obtained in an earlier experiment in which the solvent dependence of the metal-to-ligand charge-transfer band energy in $[(NH_3)_5Ru^{II}(py)]^{2+}$ was observed, it was concluded that solvent effects were dominated by the way in which specific solvent–ammine H-bonding interactions influenced the energy separation (ΔE) between the excited and ground states.[17] In that experiment E_{op} could be correlated with an empirical solvent basicity parameter, the so-called donor number, which is derived from the heat of solvation of $SbCl_5$.[18] In the decaammine dimer where ΔE = O (except for the small contribution from multiple IT transitions (Δ)), the specific solvent effect must appear in the solvent trapping term χ_s.[19] We find that multiple parameter fits of the type ($E_{op} - f$(donor number)) vs. $(1/D_{op} - 1/D_s)$ do give slightly improved correlations. In a more appropriately designed theory, specific solvent molecule–metal complex interactions may need to be included explicitly.[20]

Finally, although χ_s for D_2O falls within 3σ of the best-fit line, the positive deviation is probably significant since it appears to be a general phenomenon for mixed-valence complexes in water, independent of the ligand coordination environment.[21] We have speculated elsewhere[21] that one possible origin is in a contribution to solvent trapping from relatively high frequency solvent librations that have been observed in the Raman spectrum of water.[22]

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Registry No. BN, 100-47-0; NB, 98-95-3; Me_2SO, 67-68-5; DMF, 68-12-2; DMA, 127-19-5; PC, 108-32-7; FA, 75-12-7; NM, 75-52-5; $[(NH_3)_5Ru^{II}(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{5+}$, 54065-65-5.

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(17) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.
(18) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661.
(19) Evidence for such effects exists in related systems: Curtis, J. C., private communication.
(20) An attempt to account for such effects on a phenomenological basis has appeared: Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 1601.
(21) Hupp, J. T.; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1001.
(22) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, England, 1969; pp 242-245.

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Temperature Dependence of the Doublet Lifetime in Chromium(III) Compounds

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The role of the lowest excited doublet state in chromium(III) photochemistry has been investigated diligently for the past quarter of a century.[1,2] Among numerous reviews, that by Kemp[3] is particularly pertinent to the issues we address here. The lowest doublet, unlike excited quartet states, frequently emits detectable phosphorescence even in room-temperature aqueous solutions, which facilitates the measurement of photophysical properties and encourages experimental investigations. With the introduction of lasers and improvements in electronic detection, it is now possible to characterize a wide variety of different Cr(III) compounds including, in particular, those with short lifetimes and very low luminescence yields.

Ligand substitution reactions may occur directly from the doublet state in some, many, or all compounds, but such reactions occur in competition with other decay mechanisms. The very basic question that we address here is, Which decay process is "lifetime-controlling" under what circumstances?

Assuming conditions such that there are no diffusive bimolecular quenching processes, it is common to distinguish four decay processes: nonradiative relaxation to the ground state k_{nr}; phosphorescence k_{rad}; chemical reaction k_{rxn}; and reverse intersystem crossing RISC to an excited quartet k_{risc}. Within this model, the doublet lifetime would be expressed as

$$1/\tau_{phos} = k_{rxn} + k_{risc} + k_{nr} + k_{rad}$$

The radiative rate is extremely small and nearly temperature independent.[4] The nonradiative rate usually refers only to a weak-coupling process that can be characterized at low temperatures. It also is fairly small, and its temperature dependence is insufficient to account for the large overall decay rates at room temperature.[3] The remaining two terms are expected to be more strongly temperature dependent. Either one or the other may be invoked to explain the fact that in room-temperature solutions the doublet lifetime is usually much shorter and displays more variation with temperature than it does under cryogenic conditions. A minor detail is that RISC need not be fully irreversible; there could be some probability of return to the doublet. That does not change the logic of the model; it simply requires multiplying k_{risc} by a branching ratio.

The above scheme is logically incomplete. One should entertain the possibility of additional nonradiative pathways that dissipate electronic energy as heat but do not lead to net chemical reaction. These might involve substantial nuclear motions and be inhibited in glassy or crystalline matrices at low temperatures but assume dominance in fluid solution at ambient temperatures. Since the pioneering work of Targos and Forster[5] showing that the temperature dependence of nonradiative decay can be quite complicated, even at low temperatures, there have appeared several additional studies on the same subject, which have received critical review.[3] The relevance to room-temperature processes remains obscure. The common practice[6-11] has been to persist with the four mechanism model summarized above and argue that "if it is not reverse intersystem crossing, then it must be chemical reaction that dominates." Forster[7] certainly recognizes that the short phrase "chemical reaction" needs further elaboration; presumably others do as well. He considers the possible role of geminate recombination following a "primary" dissociative reactive step. Endicott and co-workers[12] propose a mechanism that they consider to be distinct from both nonradiative decay and chemical reaction, but which, in a way, accommodates both. They suggest a curve crossing that populates a "reactive ground-state intermediate" from which a branching is possible to form either photoproducts or the original ground state. They have in mind an associative intermediate or transition state.

Previous studies have attempted to identify processes occurring from the doublet by using a variety[3] of different kinds of mea-

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(1) Chen, S.-N.; Porter, G. B. *Chem. Phys. Lett.* **1970**, *6*, 41.
(2) Kane-Maguire, N. A. P.; Langford, C. H. *J. Am. Chem. Soc.* **1972**, *94*, 2125.
(3) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.
(4) Bjerrum, J.; Adamson, A. W.; Bostrop, O. *Acta Chem. Scand.* **1956**, *10*, 329.
(5) Targos, W.; Forster, L. S. *J. Chem. Phys.* **1966**, *44*, 4342.
(6) Shipley, N. J.; Linck, R. G. *J. Phys. Chem.* **1980**, *84*, 2490.
(7) Forster, L. S.; Castelli F. *J. Phys. Chem.* **1980**, *84*, 2492.
(8) Adamson, A. W.; Gutierrez, A. R. *J. Phys. Chem.* **1980**, *84*, 2492.
(9) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand. Ser. A* **1979**, *A33*, 53.
(10) Gutierrez, A. R.; Adamson, A. W. *J. Phys. Chem.* **1978**, *82*, 902.
(11) Zinato, E.; Adamson, A. W.; Riccieri, P. *J. Phys. Chem.* **1985**, *89*, 839.
(12) Ramasami, T.; Endicott, J. F.; Brubaker, G. R. *J. Phys. Chem.* **1983**, *87*, 5057.

0020-1669/87/1326-2334$01.50/0