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The Molecular Structures of Lifschitz Nickel(II) Complexes. I. The Preparation and Electronic Absorption Spectra of Blue and of Yellow Forms of Bis(*meso*-stilbenediamine)nickel(II) Dichloroacetate

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In this paper, the isolation of several different crystalline modifications of the Lifschitz stilbenediamine complexes of nickel dichloroacetate is described. Magnetic measurements confirm the view, later checked by X-ray crystal structure analysis (part II), that in the yellow crystals two out of three nickel atoms are paramagnetic (in octahedral coordination), while the remaining nickel atom is diamagnetic (planar coordination). Equilibrium between blue (octahedral) and yellow (planar) forms also occurs in ethanol and in acetone–water solutions of the complex. This equilibrium has been studied spectrophotometrically. The magnetic and spectroscopic data for the blue complex have been analyzed to yield values of the parameters Δ, β, and λ.

Introduction

There has been considerable speculation during the past few years[2,3] regarding the molecular structures of the Lifschitz[4] complexes of nickel and the stereochemistry of the metal ion in these compounds. These complexes, which are formed by a large number of nickel salts with *meso* and *active* 1,2-diphenylethylenediamine (stilbenediamine = stien) have the general formula $Ni(C_6H_5 \cdot CHNH_2 \cdot CHNH_2 \cdot C_6H_5)_2X_2$ and often contain solvent of crystallization. Dependent on the nature of the anion, X, and to a lesser extent on which stereoisomeric diamine is used, they exist in either a blue paramagnetic form (with $\mu_{eff} \sim 3.1$ B.M.) or a yellow diamagnetic form (or sometimes weakly paramagnetic form, with $\mu_{eff} < 2.83$ B.M.). In several instances both blue and yellow forms containing the same anion, X, are obtainable and are in some cases interconvertible.

In attempting to correlate the color, magnetism, and stereochemistry of these compounds, Pauling[5] predicted tetrahedral coordination for the nickel atom in the blue paramagnetic compounds and square-planar coordination in the yellow complexes. The suggestion of tetrahedral coordination for the paramagnetic compounds was also put forward as late as 1958 by Katzin,[3] who assumed the deep blue color of many of these to be indicative of the presence of tetrahedral nickel(II). However, it has been shown[6] from a study of the visible absorption spectra that the nickel atoms are probably octahedrally coordinated in the blue complexes, and considerations of the geometry of the ligand diamine molecules also lead to this conclusion. Several workers[7] have shown that tetrahedral complexes of nickel are usually produced when the steric and/or bonding requirements of the ligands (*e.g.*, as arises with the tertiary phosphines) make an octahedral configuration unfavorable despite the increased crystal field stabilization energy of this arrangement compared with a tetrahedral arrangement. However, in the case of ethylenediamine and related ligands, there are no "steric" reasons why tetrahedral, rather than octahedral, coordination should be favored. Comparison of the crystal field stabilization energies for the two arrangements indicates that the latter is more stable. In any event, a *regular* tetrahedral arrangement would lead to considerable distortion within the

(1) Communications regarding this paper should be directed to S. C. N., University of Keele.

(2) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(3) L. Katzin, *Nature*, **182**, 1013 (1958).

(4) (a) I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939); (b) I. Lifschitz and J. G. Bos, *Rec. trav. chim.*, **59**, 407 (1940).

(5) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, Chapter 3.

(6) C. Furlani and G. Sartori, Proceedings of Symposium on Coordination Chemistry, Rome, 1957, in *J. Inorg. Nucl. Chem.*, **8** (1958); C. Furlani, *Gazz. chim. ital.*, **88**, 279 (1958).

(7) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); L. M. Venanzi, *ibid.*, 719 (1958).

ohelate rings,[8] whereas this distortion is absent in a planar complex.

The most interesting of this series of compounds are those of the type Ni(*meso*-stien)$_2$(RCOO)$_2$, where R = H, CH$_3$, CH$_2$Cl, CHCl$_2$, and CCl$_3$, as in these cases interconversion between blue and yellow forms can be effected easily,[4] *e.g.*, by gentle heating and cooling of the solid complexes, by removal of solvent of crystallization, or by dissolution in suitable organic solvents. In the case of the dichloroacetate complex, Ni(*m*-stien)$_2$(Cl$_2$CHCOO)$_2$, blue crystals and yellow crystals can be obtained simultaneously from 95% ethanolic solutions.

These marked color changes, which are accompanied by corresponding changes in magnetic properties, are similar to those shown by several other "anomalous" nickel complexes,[9] which, diamagnetic in the solid, become paramagnetic in solution or on heating and in some cases show temperature dependent magnetic moments and spectra. Although it is now evident that one of several mechanisms is responsible for this type of behavior,[10] it is considered that, in this case, variations in color and magnetism are brought about by changes in the axial environment of the planar Ni-(stien)$^{2+}$ complex, due to the removal or addition of anions or solvent molecules,[2,11] causing a change in the tetragonality of the complex.

While much useful evidence regarding the nature of these compounds can be obtained from detailed spectroscopic and susceptibility measurements, it seemed worthwhile to carry out X-ray structure analyses of a pair of crystals, one blue and one yellow, and to study the environment of the nickel atom in each. The dichloroacetate complex was chosen for this purpose, there being certain advantages for X-ray crystal structure analysis (see part II) and, in addition, Hein and Müller[12] had extended the work of Lifschitz in studying the effects of solvents on the different blue and yellow compounds in some detail.

Results and Discussion

We have been chiefly concerned with the products obtained from acetone and from ethanol solutions, and, as reported previously,[13] have isolated three different blue crystals, (I), (II), and (III), of which the first two could be obtained from either solution, and greenish yellow crystals, which were obtained only from ethanol by slow cooling of concentrated solutions of the complex. If left in the solution, these crystals gradually dissolved and were replaced by blue crystals. At certain stages, therefore, the solution contained both blue and these "yellow" crystals side by side. Slow evaporation of ethanolic solutions at room tem-

perature gave only mixtures of the blue crystals (I) and (II), so that it may be that in solution the "yellow" crystals are the stable form above room temperature, whereas at room temperature the blue forms are stable.

The greenish yellow crystals obtained in this way were paramagnetic and dissolved in acetone and chloroform to give blue solutions. In contrast, Hein and Müller reported that the yellow crystals prepared in the above manner could not be converted into a blue modification, and that they were diamagnetic. They called such crystals yellow(I). On dehydration of previously moistened blue crystals, over P$_2$O$_5$, they obtained a greenish yellow powder, referred to as yellow-(II). This powder was weakly paramagnetic and turned blue when treated with acetone or water. Although the method of preparation is different, our greenish yellow crystals apparently correspond to the yellow(II) compound, and it seems probable that these supposedly different yellow compounds are identical. Our value for the molar susceptibility is, however, much larger than that quoted by Hein and Müller (see Experimental section) and originally determined by Lifschitz.[4a] We were unable to prepare the reputedly diamagnetic yellow(I) compound using Hein and Müller's methods; recently such a compound has been isolated, but the crystals are unstable on removal from solution.[14]

Hein and Müller noted that the blue crystals which they isolated were of variable stability on removal from solution, some becoming coated with a yellow-green powder [presumably yellow(II)] after a few hours, while others appeared stable. We have confirmed their observations and found that there are, in fact, two crystalline modifications which differ markedly in morphology and in unit cell dimensions (see Experimental section). The greater unit cell volume of crystals of the unstable blue(II) form suggests that these contain water of crystallization and that loss of this is the cause of their instability and the change from blue to yellow.

Crystals grown from acetone solution also show this variation; and from these solutions a third blue form, blue(III), has also been isolated, in addition to the crystals (I) and (II). Crystals of blue(III) are stable and appear to be unsolvated since, unlike crystals of blue(I), they do not break down to give yellow(II) powder when left under vacuum over P$_2$O$_5$.

It is not certain what conditions lead to the preferential formation of the various blue modifications from either acetone or ethanol solution, although the presence of water will obviously be one critical factor. Crystallizations under apparently the same conditions would give mixtures of blue(I) and blue(II) in varying amounts, or sometimes all of one kind—there appeared to be no easy way of controlling the experiment to give a specific product.

Electronic Spectra.—As ethanolic solutions of the dichloroacetate complexes yield both blue and yellow

(8) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(9) J. B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947).

(10) F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2818 (1961); L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *ibid.*, **82**, 3487 (1960).

(11) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(12) F. Hein and H. Müller, *Z. anorg. allgem. Chem.*, **283**, 172 (1956).

(13) W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Proc. Chem. Soc.*, 297 (1961).

(14) D. M. L. Goodgame, private communication.

crystals, it seemed worthwhile to compare the absorption spectra of these solutions with those of the blue complex and with that of a yellow and authentically diamagnetic complex, such as Ni(*meso*-stien)$_2$Cl$_2$. Furlani[6] has previously measured the spectra of some of these complexes in various solvents and noted the "mixed" appearance of the spectra in alcohols; however, he does not report the extinction coefficients of the various bands, which are useful in enabling a comparison with the spectra of other nickel(II) complexes to be made.

The results of the measurements made during the course of this work are given in Tables I and II. Within experimental error, the different crystalline yellow and blue complexes give identical spectra in the same solvent; there are differences in solvent of crystallization, but in the dilute solutions used these differences have no effect on the spectra.

TABLE I
ELECTRONIC ABSORPTION SPECTRA

| | —Absorption maxima— | | |
Medium	mμ	cm.$^{-1}$	ϵ_{max}
(a) Ni(*m*-stien)$_2$(Cl$_2$CHCOO)$_2$			
Acetone (and chloro-	970	10,300	6.5
form)	790	12,650	3.5
	600	16,700	7.0
	~370 (sh)	~27,200	12.0
95% ethanol	970	10,300	5.5
	780	12,800	3.0
	600	16,700	6.5
	443	22,600	24.0
	373	26,900	16.0
(b) Ni(*m*-stein)$_2$Cl$_2$			
95% ethanol	445	22,500	66.0

TABLE II
ABSORPTION SPECTRA OF AQUEOUS ACETONE SOLUTIONS OF
Ni(*m*-stien)$_2$(Cl$_2$CHCOO)$_2$

H$_2$O concn., M	16,700 cm.$^{-1}$	18,100 cm.$^{-1}$	22,600 cm.$^{-1}$
		ϵ_{mol}	
0	6.9	4.4	1.8
6	6.5	4.45	9.8
14	6.0	4.4	18.2
24	5.1	4.4	29.4
36	4.2	4.35	48.2

The spectra of the complexes in acetone and chloroform solution show great similarity to those of other octahedral complexes of Ni(II),[15] and the observed band intensities indicate the extreme unlikelihood of the presence of tetrahedral Ni(II). As expected, the spectra of ethanolic solutions show absorption bands common to both the spectrum of the blue complex (*i.e.*, as given by acetone or chloroform solution) and to that of the yellow diamagnetic complex Ni(*m*-stien)$_2$Cl$_2$. This "mixed" appearance therefore suggests the presence in the solution of both the (planar) yellow complex and a blue (octahedral) complex and, probably, an equilibrium between them.

To clarify this point, the effect of the addition of

water to a solution of the complex in acetone was studied, since the presence of water is known to favor the formation of the yellow complex in solution. From the results in Table II, it is seen that this addition is accompanied by the appearance in the spectrum of the absorption maximum at 22,600 cm.$^{-1}$, characteristic of the yellow form, and that as the concentration of water is increased, the spectrum approaches that of the yellow chloride complex. In the intermediate stages (water:acetone ratio *ca.* 1:2) the spectrum approximates very closely to that of the ethanolic solution, so it seems reasonable to assume that the two solutions contain identical complex species. The occurrence of the isosbestic point in the aqueous acetone solutions at 18,100 cm.$^{-1}$ indicates the presence of only two such species in the solutions and the equilibrium between these two species may therefore be written

$$\text{Ni}(m\text{-stien})_2(\text{Cl}_2\text{CHCOO})_2 + \text{H}_2\text{O} \rightleftharpoons$$
$$\text{Ni}(m\text{-stien})_2{}^{2+} + 2(\text{Cl}_2\text{CHCOO})^- \quad (1)$$
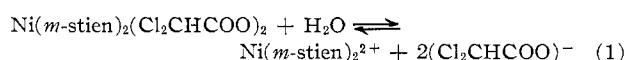
which, as previously reported,[13] is supported by the observation that addition of sodium dichloroacetate depresses the prominent peak at 22,600 cm.$^{-1}$. Taking the value of the molar extinction coefficient at 22,600 cm.$^{-1}$ as a measure of the amount of yellow complex present in solution, the value of 24 found for this band in the spectra of ethanolic solutions of the complex at room temperature (*ca.* 20°) indicates that approximately one third (34%) of the complex in these solutions is present as the yellow diamagnetic form (the value of 66, observed for the chloride complex, being taken to indicate 100% yellow form).

Turning to the yellow(II) form, crystals of which are grown from saturated ethanolic solutions, the value of 2.58 B.M. obtained for the magnetic moment of these crystals is indicative of a ratio of paramagnetic octahedral to planar diamagnetic molecules of 2:1 in the solid complex, the moment of each paramagnetic nickel ion thus being 3.16 B.M. This result has been substantiated by studies of the crystal spectra[16] and verified unambiguously by a detailed X-ray crystal structure analysis, to be described in part II.

Although in the equilibrium summarized in eq. 1 it was assumed that the blue complex has dichloroacetate ions coordinated directly to the nickel ion, the X-ray structure analysis of the blue(I) crystals (to be described in part II) indicates that this blue form has water molecules coordinated to the nickel ion, so it might be thought that addition of water would cause this modification to be formed. However, it appears from the above results that the blue complexes are stable only in solvents of low dielectric constant, and that as the latter is increased, *e.g.*, by the addition of water, dissociation is brought about and the anions or water molecules are removed, leaving a planar or strongly tetragonal yellow complex. Therefore it seems that in aqueous solution the axial positions of the planar complex Ni(stien)$_2{}^{2+}$ are sterically hindered, thus preventing the close approach of anions or solvent

(15) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); *ibid.*, **10**, 887 (1956).

(16) C. R. Hare, private communication.

molecules, and that this steric hindrance (and hence ready formation of yellow complex) is caused by the geometrical properties of the *meso* diamine. This is supported by the observation that yellow complexes are not readily obtainable with the *racemic* diamine and that such complexes give blue aqueous solutions.[4b]

Since the six coordinated groups are not of one kind, it might be expected that the absorption bands for the blue complex would show some evidence of deviation of the ligand field from purely O_h symmetry and that the spectrum could be interpreted using the results calculated by Maki[17] for hexacoordinated Ni(II) complexes of D_{4h} symmetry. However, the main absorption bands do not show the presence of any shoulders, or pronounced asymmetry,[18] which would be indicative of tetragonal splitting, so it can be assumed that the latter must be fairly small. Assignment of the absorption bands can thus be carried out[6] assuming O_h symmetry and using the rule of average environment[19]; *i.e.*, Δ, the ligand field strength parameter, is found by interpolation between Δ values for the complexes with six equal ligand atoms.

The three main bands, which occur at 10,300, 16,700, and 26,900 cm.$^{-1}$, are thus assigned to the three spin-allowed transitions, now well established for the majority of octahedral Ni(II) complexes,[15] namely, $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1); $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2); and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3). The value of ν_1 gives Δ directly (except where this has to be corrected for intermediate coupling due to interaction between $^3T_{2g}(F)$ and $^1E_g(D)$) and so the latter can be taken to be 10,300 cm.$^{-1}$. To obtain satisfactory agreement between experiment and theory for the energies of the bands ν_2 and ν_3, it is necessary to assume that the ^3F–^3P term distance in the complex is reduced from its free ion value.[15] For Ni(II), this term separation is $15B$, where B, the Racah interelectronic repulsion integral, has the value 1041 cm.$^{-1}$ in the free ion. The effective value, B', in the complexed ion can be found from the diagonal sum rule,[20] $15B' = \nu_3 + \nu_2 - 3\Delta$, and for the blue complex is calculated to be 846 cm.$^{-1}$. The ratio of the two values, β, of 0.81, is comparable to those obtained for other octahedral nickel complexes.[20] Using these values of B' and Δ, the energies of the ν_2 and ν_3 bands can be calculated and checked against the observed values, since the justification for treating the complex as having cubic symmetry is that the three spin-allowed bands can be described in terms of these two parameters.

Since they have the same symmetry, the two $^3T_{1g}$ components, arising from the ^3F and ^3P levels, will interact, and allowing for this, their energies can be shown, by either the weak-field or the strong-field approach, to be $(7.5B' + 0.3\Delta) \pm {}^1/_2[(15B')^2 - 18B'\Delta$

$+ \Delta^2]^{1/2}$, the energy of the ground state, $^3A_{2g}$, being -1.2Δ. The calculated values of ν_2 and ν_3 are thus 16,550 and 27,050 cm.$^{-1}$, in favorable agreement with the experimental values, and suggesting little distortion from O_h symmetry.

In addition to the three spin-allowed bands, the spectrum of the blue complex shows a weaker band, not reported by Furlani,[6] at 12,650 cm.$^{-1}$. Using the "complete" energy level diagram for Ni(II),[21] this can be assigned to the spin-forbidden transition from the ground state, $^3A_{2g}$, to the singlet, $^1E_g(D)$, which is intermixed with $^3T_{2g}$ and $^3T_{1g}$ under the action of spin–orbit coupling. The intensity of the band is thereby enhanced.

The reduction of the Racah parameter, B, from its free ion value is often taken as evidence of appreciable covalence in the metal–ligand bonds in complexes, and the reduction of the spin–orbit coupling constant, λ, as calculated from magnetic data, has been attributed to the same cause.[22] When the ground state is an orbital singlet, deviations from the spin-only value can be ascribed to the "mixing" in of higher states having the same multiplicity, under the action of spin–orbit coupling. These deviations become appreciable in Ni(II) complexes, where λ is large. Using the corrected susceptibility for the blue complex, and subtracting out the temperature independent part (given by $8N\beta^2/\Delta$), a value for the Landé g factor of 2.18 is obtained. Using the equation $g = 2(1 - 4\lambda'/\Delta)$, λ' is calculated to be 230 cm.$^{-1}$, considerably reduced from the free ion value of 315 cm.$^{-1}$.

Assuming that the ligand field strength of stilbenediamine is the same as that for ethylenediamine, namely 11,500 cm.$^{-1}$,[15] then according to the rule of average environment, if dichloroacetate ions are coordinated to the nickel in the blue complex, one might expect a lower value than 10,500 cm.$^{-1}$, which is that observed for Δ in the complex Ni(en)$_2$(H$_2$O)$_2$.[15] Although a lower value is actually observed, the difference is fairly small, and it is probably unwise to attach too much significance to it, as the uncertainty in the experimental value could be as large as the difference.

The spectrum of the yellow diamagnetic chloride complex, and presumably also the true yellow dichloroacetate complex, showing the single absorption maximum at 22,600 cm.$^{-1}$ is more difficult to interpret. Since the complex is diamagnetic, the ground state will be a singlet, and Maki[17] has shown that in planar Ni(II) complexes of D_{4h} symmetry the $^1A_{1g}$ state arising from the ^1D level in the free ion becomes the ground state at high values of ligand field strength. She concludes that even a small axial perturbation will destabilize this singlet state and stabilize the $^3B_{2g}$ (F) state, so this becomes the ground state and the complex is paramagnetic. Assuming D_{4h} symmetry, the observed band can probably be assigned to the transition $^1A_{1g} \rightarrow {}^1A_{2g}(G)$, although the agreement

(17) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(18) The band at high energy is masked by charge-transfer bands at the beginning of the ultraviolet region so that no conclusions regarding possible asymmetry can be drawn.

(19) C. K. Jørgensen, "Energy Levels of Complexes and Gaseous Ions," Gjellerups, Copenhagen, 1957.

(20) O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

(21) C. J. Ballhausen and A. D. Liehr, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

(22) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

between the experimental value and the value calculated from a simple crystal field model, as with other planar nickel(II) complexes, is poor.[6]

It is thus fairly evident from the spectroscopic and magnetic data presented here that the explanations of the properties of these compounds put forward by Ballhausen and Liehr and Maki are essentially correct. These predictions have subsequently received conclusive confirmation from the X-ray crystal structure analyses to be described in part II.

Experimental

Preparation of Compounds.—*meso*-Stilbenediamine was prepared by the method due to Mills and Quibell[23]; m.p. 119° (lit.[23] 119.5°). The bis-*meso*-stilbenediamine nickel(II) dichloroacetate complex was prepared as a blue-gray precipitate, by mixing a dilute aqueous solution of nickel dichloroacetate with a concentrated solution of the diamine in 95% ethanol. If the concentration ratios of water and ethanol were reversed, the complex separated out as greenish yellow crystals [yellow(II)] after ∼24 hr.

Anal. Calcd. for the unsolvated complex: C, 51.9; H, 4.6; N, 7.58; Cl, 19.25. Found (blue(I) crystals): C, 47.27; H, 5.30; N, 7.06; Cl, 17.30. Calcd. for Ni(stien)₂(Cl₂CHCOO)₂· 4H₂O, subsequently found to be correct from the structure analysis: C, 47.3; H, 5.16; N, 6.9; Cl, 17.50. No analyses were carried out on the unstable blue(II) crystals. Found (yellow(II) crystals): C, 50.72; H, 5.05; N, 7.14; Cl, 17.79. The formula found from the X-ray crystal structure analysis is 3[complex]·2C₂H₅OH·4H₂O, which gives calculated values C, 50.42; H, 5.12; N, 7.06; Cl, 17.89.

Unit Cell Dimensions.—Both blue(I) and blue(II) crystals belong to the monoclinic system and their cell dimensions are, respectively: $a = 14.98$, $b = 11.34$, $c = 11.64$ Å., $\beta = 109.5°$, $V = 1862$ Å.³, and $a = 14.6$, $b = 12.2$, $c = 13.1$ Å., $\beta = 119°$, $V = 2041$ Å.³. These dimensions were determined from oscillation and zero-level Weissenberg photographs.

Magnetic Measurements.—Bulk susceptibility measurements were made at room temperature, using a Gouy balance. The

Gouy tube was calibrated with HgCo(NCS)₄ using the data of Figgis and Nyholm.[24] All measurements were carried out twice, the duplicate measurements involving a repacking of the tube. The results are given in Table III, the diamagnetic corrections quoted being computed from Pascal's constants.[25]

Table III

	T, °K.	$\chi_m \times 10^6$	Diamag. cor. $\times 10^6$	μ_{eff}, B.M.
Blue(1)				
Ni(*m*-stien)₂(Cl₂CHCOO)₂· 4H₂O	297	3714	−454	3.16 ± 0.05
Yellow(II)				
Ni(*m*-stien)₂(Cl₂CHCOO)₂· ²/₃C₂H₅OH·⁴/₃H₂O	297	2370	−443	2.58 ± 0.05

Lifschitz[4a] reports a value of 3740×10^{-6} c.g.s. unit for the molar susceptibility of the anhydrous blue complex. Including a diamagnetic correction of -402×10^{-6} c.g.s. unit, and assuming a temperature of 20°, this leads to a value for μ_{eff} of 3.13 B.M., which is in good agreement with the above value. However, the value obtained for the yellow(II) in powder form was 890×10^{-6} c.g.s. unit; including a diamagnetic correction, this gives $\mu_{eff} = 1.76$ B.M., which is much lower than that reported above for the yellow(II) crystals.

Electronic Spectra.—The solution spectra were measured on a Unicam S.P. 500 spectrophotometer over the range 10,000–33,000 cm.⁻¹, using absolute and 95% ethanol, analytical grade chloroform, and acetone (dried over potassium carbonate and redistilled).

(23) W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.*, 839 (1935).

(24) B. N. Figgis and R. S. Nyholm, *ibid.*, 4190 (1958).

(25) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960.