—A 0.50-g sample of bis(N-isopropyl-β-mercaptoethylamine)-nickel(II) (0.0017 mole) and 0.62 g of nickel(II) perchlorate hexahydrate (0.0017 mole) were placed in 150 ml of methanol and stirred at room temperature for 2 hr. Water (15 ml) was added and the reaction was allowed to proceed for an additional 2 hr. Filtration of the reaction mixture yielded 0.58 g of the product (81%). The maroon solid was dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $\{Ni[Ni(C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$: C, 28.33; H, 5.71; N, 6.61; S, 15.31; Cl, 8.36. Found: C, 27.89; H, 5.80; N, 6.98; S, 14.66; Cl, 7.99.

General Preparative Procedure for Tetrakis(N-substituted β-mercaptoethylamine)trinickel(II) Complex Cation.—The synthetic procedures for the preparation of tetrakis(N-isopropyl-β-mercaptoethylamine)trinickel(II) chloride, tetrakis(N-*n*-octyl-β-mercaptoethylamine)trinickel(II) perchlorate, and tetrakis(N-*n*-hexyl-β-mercaptoethylamine)trinickel(II) perchlorate involved the reaction of the bis(N-substituted β-mercaptoethylamine)-nickel(II) complex with twofold excess of nickel(II) salt. The salt may contain a convenient precipitating anion or the anion may be added to the reaction mixture separately as the sodium salt. Perchlorate ion proved to be an excellent choice for obtaining crystalline products. When the ligand has a very bulky amine function, as with N,N-diethyl- and N-*t*-butyl-β-mercaptoethylamine, this procedure will not yield the trinuclear complex.

Preparation of Tetrakis(N-*n*-propyl-β-mercaptoethylamine)dinickel(II)palladium(II) Perchlorate, $\{Pd[Ni(n\text{-}C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$.—A 1.00-g sample of bis(N-*n*-propyl-β-mercaptoethylamine)nickel(II) (0.0034 mole) was suspended in 10 ml of water. To this suspension, 0.537 g of potassium tetrachloropalladate(II) (0.0017 mole) in 10 ml of water was added. The reaction mixture gradually became blood red. After stirring for 90 min at room temperature, the mixture was filtered to remove any undissolved reactant. A solution of 0.98 g of sodium perchlorate monohydrate (0.007 mole) in 15 ml of water was added to the filtrate precipitating the brick red complex salt which was isolated by filtration and dried *in vacuo* over $Mg(ClO_4)_2$; yield, 1.01 g (68.5%). *Anal.* Calcd for $\{Pd[Ni(C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$: C, 26.82; H, 5.40; N, 6.26; S, 14.32; Cl, 7.92. Found: C, 27.04; H, 5.19; N, 6.12; S, 14.33; Cl, 7.75.

Acknowledgment.—This investigation was supported by the U. S. Army Research and Development Command.

CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Electronic Structure of Tetragonal Nickel(II) Complexes[1a]

BY DAVID A. ROWLEY[1b] AND RUSSELL S. DRAGO

Received October 18, 1967

The electronic spectra of tetragonal nickel(II) complexes have been studied for a variety of axial and equatorial ligands. The spectra contain a large number of bands permitting us to test previously reported approximations that have been used in calculation of the crystal field parameters Ds and Dt. The results show that, contrary to the approach usually made, all off-diagonal matrix elements must be considered when calculating these parameters. Significant errors exist in many literature values. Data are presented to show that for tetragonal nickel(II) complexes, the value Dq^z does not remain constant on going from complex to complex when the in-plane field changes. The values of Dq^z become less as the in-plane field becomes stronger. This is explained on the basis of a ligand inductive effect. Other manifestations of this phenomenon are discussed. The values for the McClure parameter, $\delta\pi$, are interpreted on the basis of two alternative effects: π-electron repulsion (π*-antibonding effects) and metal-to-ligand π bonding.

Introduction

Recently there has been considerable interest[2–9] in the assignment of spectra of tetragonal metal complexes and the interpretations of the ligand field parameters Ds and Dt[3a,4–8] or $\delta\sigma$ and $\delta\pi$.[2] This has been in part stimulated by the pioneering work of Wentworth and Piper.[3] Invariably, the number of bands in the experimental spectra is equal to or less than the number of parameters to be fit (Dq, B, Ds, and Dt). Consequently any reference to configuration interaction (^3F and ^3P interaction) and off-diagonal crystal field matrix elements (interaction of ^3E_g states arising from ^3F) has been ignored or assumed to be small. In the course of our studies on tetragonal nickel(II) complexes,[4,10] we found that the electronic spectra contained a large number of bands. We therefore thought it desirable to examine in detail the method of calculation of the crystal field parameters, for we had enough bands to evaluate the parameters and test the model. We carried out the calculations with the inclusion of all off-diagonal matrix elements and compared these results with those obtained by using the approximations employed by others.[2,3,8] The systems chosen for this work were of the form $Ni(L)_4X_2$ where $(L)_4$ represents four individual ligands, two bidentate

---

(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) Abstracted in part from the Ph.D. thesis of D. A. Rowley, University of Illinois, 1968. National Institutes of Health Predoctoral Fellow 1967–1968.

(2) D. S. McClure in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 498.

(3) (a) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965); (b) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 1524 (1965).

(4) D. A. Rowley and R. S. Drago, *ibid.*, **6**, 1092 (1967).

(5) A. B. P. Lever, "Werner Centennial," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 430.

(6) D. M. L. Goodgame, M. Goodgame, M. A. Mitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

(7) W. A. Baker and M. S. Phillips, *ibid.*, **5**, 1042 (1966).

(8) G. R. Brubaker and D. H. Bush, *ibid.*, **5**, 2114 (1966).

(9) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *J. Chem. Soc., Sect. A*, 1769 (1966).

(10) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

TABLE I

ELECTRONIC SPECTRAL DATA AT 77°K

Compound	Transition,[c] cm^{-1}							
	$^3B_{1g} \rightarrow {}^3E_g$	$\rightarrow {}^3B_{2g}$	$\rightarrow {}^1A_{1g}, {}^1B_{1g}$	$\rightarrow {}^3A_{2g}(^3F)$	$\rightarrow {}^3E_g\ (^3F)$	$\rightarrow {}^1\Gamma$	$\rightarrow {}^3A_2\ (^3P)$	$\rightarrow {}^3E_g\ (^3P)$
Ni(S-dmeen)$_2$Cl$_2$	8,510	12,110	12,900	14,370	17,410	...	~25,600[a]	27,340
Ni(S-dmeen)$_2$Br$_2$	7,920	12,300[a]	*a*	13,410	17,450	...	...	27,950
Ni(S-dmeen)$_2$(DMSO)$_2$(BF$_4$)$_2$	8,880	12,450	13,290	14,870	17,750	...	~26,300[a]	28,000
Ni(S-dmeen)(DMF)$_2$(BF$_4$)$_2$	10,120	12,420	13,270	...	17,930	...	...	28,740
Ni(py)$_2$Br$_2$	8,300	6,040	...	14,240	~12,800[a]	20,300	23,910	22,640
Ni(az)$_4$Cl$_2$[b]	8,375	11,890	12,800	13,870	17,150	...	...	27,200

[a] Shoulder on main peak. [b] This sample was provided by Professor Charles Root, Bucknell University; az = aziridine. [c] The error limits are ±80 cm^{-1}.

TABLE II

CALCULATED AND OBSERVED SPECTRA (CM^{-1}) FOR SELECTED COMPLEXES AT 77°K

Ni(py)$_4$(ClO$_4$)		Ni(py)$_4$(BF$_4$)$_2$		Ni(Temp a)Cl$_2$		Ni(py)$_2$Cl$_2$		Transition
ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	
7,870 ± 50	7,920	7,580 ± 90	7,520	8,490 ± 50	8,470	8,620 ± 40	8,680	$^3B_{1g} \rightarrow {}^3E_g(^3F)$
12,920 ± 70	12,890	13,050 ± 50	13,070	14,730	14,260	6,270 ± 80	6,290	$\rightarrow {}^3B_{1g}(^3F)$
...	13,990	...	13,230		14,550	14,490 ± 40	14,530	$\rightarrow {}^3A_{2g}(^3F)$
13,610 ± 70	...	13,890 ± 70	...		...	...	...	$\rightarrow {}^1A_{1g}, {}^1B_{2g}(^1D)$
17,390 ± 70	17,440	17,620 ± 70	17,680	19,030 ± 80	19,040	13,300[a]	13,410	$\rightarrow {}^3E_g(^3F)$
25,600[a]	25,850	26,000[a]	26,050	27,000[a]	27,150	24,700 ± 40	24,750	$\rightarrow {}^3A_{2g}(^3P)$
27,700 ± 50	27,660	28,240 ± 80	28,170	28,840 ± 80	28,880	23,400 ± 50	23,340	$\rightarrow {}^3E_g(^3P)$

[a] Shoulder on main band.

chelates, or a cyclic tetradentate ligand. The site symmetry was assumed to be D_{4h} and the electronic spectra fit this model. The particular complexes were chosen so that the number of electronic transitions observed was greater than or equal to the number of crystal field parameters.

It has previously been proposed[3] that the *Dq* of the axial ligand is often transferable from complex to complex, and it was of interest to test this proposal when all off-diagonal interaction is considered. We conclude that this is often not correct and propose a model based on the inductive properties of the ligands to predict the direction of the deviation.

Finally, this study allows us to obtain values for McClure's[2] $\delta\pi$ and $\delta\sigma$ parameters calculated with and without configuration interaction to see if any differences result. This is significant since spectral bands have been assigned on the basis of the signs and relative magnitudes of $\delta\pi$ and $\delta\sigma$.[7,9]

Experimental Section

The following compounds were prepared as described in the literature: Ni(py)$_4$(ClO$_4$)$_2$,[10] Ni(py)$_4$(BF$_4$)$_2$,[10] Ni(py)$_4$Br$_2$,[2] Ni(py)$_2$Cl$_2$,[11] and Ni(Temp a)Cl$_2$.[12] In all instances elemental analyses confirmed that we had prepared the compound sought.

Ni(py)$_2$Br$_2$ was prepared by washing Ni(py)$_4$Br$_2$ several times with a 50–50 mixture of ether and chloroform. The product was air dried on the filter. *Anal.* Calcd for Ni(C$_5$H$_5$N)$_2$Br$_2$: C, 31.9; H, 2.68. Found: C, 32.2; H, 2.95.

Ni(S-dmeen)$_2$X$_2$ complexes, where S-dmeen is N,N′-dimethylethylenediamine and X$^-$ = Cl$^-$, Br$^-$, were prepared in the following manner. A 0.01-mol sample of the appropriate hydrated nickel salt was dehydrated in dimethoxypropane (DMP) and methanol. After 2 hr, 0.05 mol (6 ml) of S-dmeen was added. After stirring for 3 hr, the complex was collected, washed with absolute ethanol and ether, and then dried *in vacuo* overnight. *Anal.* Calcd for Ni(C$_6$H$_{12}$N$_2$)$_2$Cl$_2$: C, 31.4; H, 7.91; N, 18.3; Ni, 19.2. Found: C, 31.4; H, 7.87; N, 18.2; Ni, 19.4. Calcd for Ni(C$_6$H$_{12}$N$_2$)$_2$Br$_2$: C, 24.3; H, 6.13; N, 14.2; Ni, 14.9. Found: C, 24.2; H, 6.07; N, 13.3; Ni, 15.1.

Complexes of the form Ni(S-dmeen)L$_2$(BF$_4$)$_2$, where L is dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), were prepared by dehydrating 0.01 mol (3.38 g) of Ni(H$_2$O)$_6$(BF$_4$)$_2$ with DMP and then adding 0.05 mol of S-dmeen. After addition of 0.10 mol of the appropriate ligand, DMSO (7 ml) or DMF (8 ml), precipitation with ether yielded an oil. The oil was dissolved in a minimum amount at absolute ethanol and 5 drops of S-dmeen, DMP, and DMSO or DMF were added. After addition of ether, the resultant oil was stirred for 2 hr, and the solid was collected and washed with ether. The compound was then dried *in vacuo* overnight. The final collection and washing was done in a drybox since the compounds were slightly hygroscopic. *Anal.* Calcd for Ni(C$_6$H$_{12}$N$_2$)$_2$(C$_2$H$_6$SO)$_2$(BF$_4$)$_2$: C, 25.5; H, 6.42; N, 9.92; Ni, 10.4. Found: C, 25.5; H, 6.53; N, 9.90; Ni, 10.4. Calcd for Ni(C$_6$H$_{12}$N$_2$)$_2$(C$_3$H$_7$NO)$_2$(BF$_4$)$_2$: C, 30.3; H, 6.90; N, 15.2; Ni, 10.6. Found: C, 29.8; H, 6.98; N, 14.4; Ni, 10.7.

Spectrophotometric Measurements.—Mull spectra were recorded on a Cary Model 14RI spectrophotometer. The samples were mounted in a dewar filled with liquid nitrogen. The temperature of the dewar was allowed to equilibrate for about 20 min. Mulls were prepared by grinding the compounds in either Nujol or Kel-F stopcock grease and then placing the mixture between two glass plates on the sample mount of the dewar. A piece of filter paper soaked with Nujol was placed in the reference beam. The region from 3300 to 17,500 Å was scanned.

Calculations.—The calculations employed to fit the spectra have previously been described.[4]

Results and Assignments

The spectral data that we have obtained at liquid nitrogen temperatures are shown in Tables I and II. The relationship between the free-ion octahedral and tetragonal field splitting of the d orbitals is illustrated in Figure 1. The assignments and calculations for the Ni(S-dmeen)$_2$L$_2$(BF$_4$)$_2$ and Ni(S-dmeen)$_2$X$_2$ are straightforward, and the results are shown in Table III.

The assignment of the spectra of Ni(py)$_4$X$_2$, where X$^-$ = ClO$_4^-$ or BF$_4^-$, and Ni(Temp a)Cl$_2$ becomes

---

(11) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

(12) (a) N. F. Curtis, *ibid.*, 2644 (1964); (b) Temp a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetaazacyclotetradecane.

TABLE III

RESULTS OF CALCULATIONS—VALUES FOR THE SPECTROCHEMICAL PARAMETERS (cm^{-1})

Compound	Spectrochemical Parameters						
	B	Dq^{xy}	*Ds*	*Dt*	Dq^z	$\delta\pi$	$\delta\sigma$
$Ni(S\text{-}dmeen)_2Cl_2$	853	1215	847	356	591	−380	−1950
$Ni(S\text{-}dmeen)_2Br_2$	884	1230	1186	416	502	−740	−2560
$Ni(S\text{-}dmeen)_2(DMSO)_2(BF_4)_2$	863	1245	802	355	625	−315	−1870
$Ni(S\text{-}dmeen)_2(DMF)_2(BF_4)_2$	867	1242	293	246	822	+175	−900
$Ni(py)_4(ClO_4)_2$	869	1289	930	500	410	−145	−2330
$Ni(py)_4(BF_4)_2$	890	1307	1240	540	360	−510	−2870
$Ni(py)_2Cl_2$	841	629	−598	−330	1210	+72	+1520
$Ni(py)_2Br_2$	810	594	−637	−345	1200	+87	+1680
$Ni(Temp\ a)Cl_2$	840	1426	1100	574	420	−215	−2730
$Ni(py)_4Cl_2$	820	1173	480	283	680	−10	−1240
$Ni(py)_4Br_2$	810	1150	635	316	600	−156	−1540
$Ni(az)_4Cl_2$	854	1191	940	347	585	−542	−2060

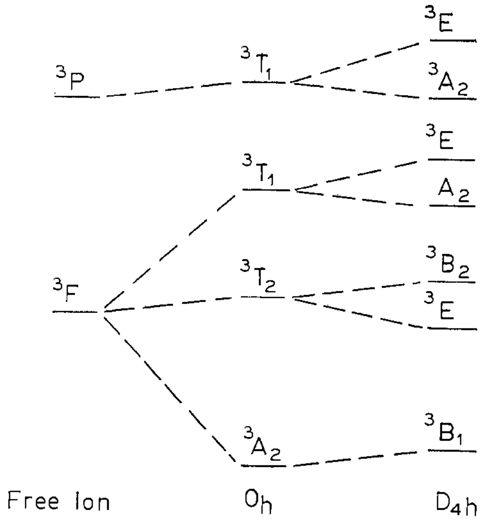

Figure 1.—Correlation diagram for the triplet states of a d^8 configuration. The subscript g has been left off for states in O_h and D_{4h} for clarity in presenting the diagram.

much more complicated than those previously reported,[4] because of the uncertainty of the exact location of the $^3A_{2g}(^3F)$ and $^3B_{2g}(^3F)$ transitions due to partial overlap of these bands with each other and the low-energy spin-forbidden bands.

If we consider $Ni(py)_4(ClO_4)_2$ as a representative example, our assignments proceed as follows. The spectrum shown in Figure 2 indicates that we have three bands that we can assign confidently: $^3E_g(^3T_{2g})$, $^3E_g(^3T_{1g}, {}^3P)$, and $^3E_g(^3T_{1g}, {}^3F)$. In making these assignments and assigning the lower energy component of the band envelope located between 12 and 16 kK to the $^3B_{2g}$ transition (see Figure 2), the calculated positions of the assigned transitions all agree within experimental error (see Table II). However, the calculated position of the $^3A_{2g}$ transition (13.99 kK) which arises from the ^3F term does not agree well with the other maximum of the band located between 12 and 16 kK. Under high resolution of the spectrophotometer, the high-energy peak of this band envelope consists of two relatively sharp components, which indicates that these are the transitions to the low-energy singlet states. These transitions lie on top of the $^3A_{2g}$ transition obscuring the maxima for this transition. We therefore suggest that the band envelope in the near-infrared region contains four transitions (two spin allowed and two spin forbidden).

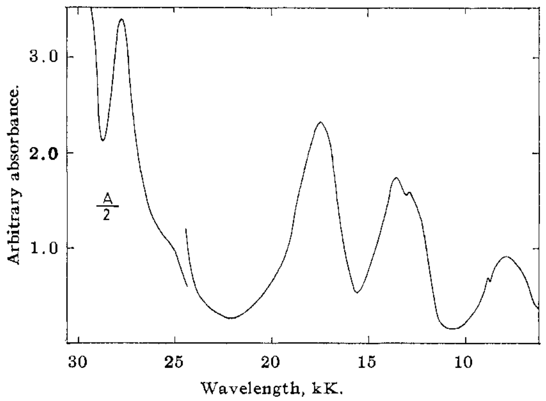

Figure 2.—Mull spectrum of $Ni(py)_4(ClO_4)_2$ at liquid nitrogen temperature.

In addition to the agreement between our calculations and experimental results for the four transitions we have assigned, the sixth spin-allowed band $^3A_{2g}$ ($^3T_{1g}$, ^3P) is predicted to occur about 25.85 kK and there is a shoulder on the highest energy band of about 25.60 kK. This confirms our earlier assignments[4] in which we predicted the sixth band to be located on the low-energy side of the highest spin-allowed d–d transition. Therefore, experimental results and calculations support our assignments presented in Table II.

The assignment of the spectrum of $Ni(py)_4(BF_4)_2$ proceeds along similar lines. Again, there is a band envelope in the 12–16-kK region which contains two distinct peaks. Assigning the lower energy band to the $^3B_{2g}$ transition, agreement between calculation and theory is obtained. No other assignment will lead to agreement with experiment. The results are presented in Table II.

Assigning the spectrum of $Ni(Temp\ a)Cl_2$ was a little more difficult, since we had a very broad asymmetric band centered at 14,700 cm^{-1} (see Figure 3). A shoulder was evident on the low-energy side suggesting the $^3B_{2g}$ transition was at a lower energy than 14,700 cm^{-1}. Accordingly, the three known transitions were assigned, and the $^3B_{2g}$ transition was allowed to vary over a 1000-cm^{-1} range until a fit was reached. The

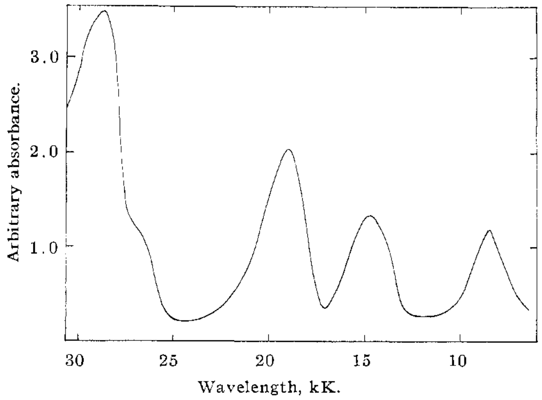

Figure 3.—Mull spectrum of Ni(Temp a)Cl_2 at liquid nitrogen temperature.

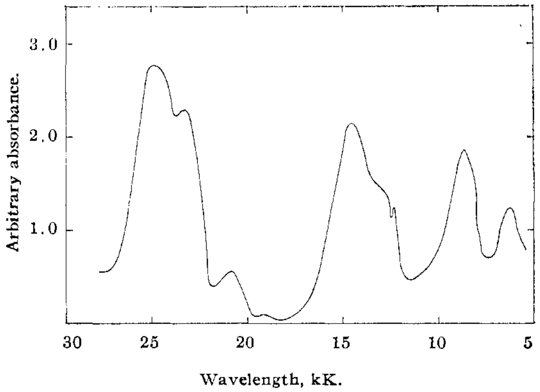

Figure 4.—Mull spectrum of $Ni(py)_2Cl_2$ at liquid nitrogen temperature.

final data are presented in Table II. It is seen that $^3E_g(^3T_{2g},{}^3F)$ and $^3B_{2g}$ are very close together in agreement with the observed broad band in this region. The other three transitions all agree favorably.

The room-temperature reflectance spectra of $Ni(py)_2Cl_2$ and $Ni(py)_2Br_2$ have been reported.[11] However, at 77°K resolution of the spectra was improved considerably so that all six spin-allowed transitions could be seen, as is shown in Figure 4. We attempted to fit the spectra of these compounds assuming that they had the symmetry D_{4h}. Actually, the structure contains bridging halogens and six-coordinate nickel(II), but the symmetry is C_i[13] because of distortions of the halogens from planarity. We assigned the spectra by reversing the orderings of the ^3E_g and $^3B_{1g}$ as well as ^3E_g and $^3A_{1g}$ states (arising from the T states) compared with those assigned for the $Ni(py)_4Cl_2$ spectrum. In $Ni(py)_2Cl_2$ we now have the strong axial field and weak in-plane field. When calculations were performed, "exact" agreement was not obtained, but in view of the symmetry this is not surprising. The observed and calculated spectra are shown in Tables I and II.

In Table III, we have presented the results of our calculations. In all cases when there is an independent check available (at least five bands observed), these values give the observed transition energies within experimental error except where noted.

The extension of our calculations to include spin–orbit coupling would be desirable, but since no fine structure in the observed transitions was detected, the results would have little meaning. The splittings that we observe in these complexes are too large to be explained by the spin–orbit splitting of the transitions in octahedral d^8 complexes. Liehr and Ballhausen[14] have shown that the effect of including spin–orbit coupling in octahedral complexes is to change the center of gravity of the transition by less than 1%. Therefore spin–orbit coupling was neglected.

Discussion

When the electronic spectrum does not contain as many bands as found in the systems reported here, several approximations must be made in order to evaluate the ligand field parameters. In one approach,[3] Dq^{xy} is assumed to be the same as that for the ligand in the octahedral complex $Dq(O_h)$. All configuration interaction and off-diagonal matrix elements are ignored in the evaluations of Dt. In a second approach,[8] Dq^{xy} is obtained directly from the spectra of the tetragonal complex but Dt (and hence Dq^z) is evaluated without inclusion of configuration interaction or off-diagonal crystal field matrix elements. We are now in a position to evaluate the error in these approaches.

First consider Dq^{xy} for $Ni(S\text{-}dmeen)_2X_2$ and $Ni(py)_4X_2$. The similarity of Dq^{xy} and $Dq(O_h)$ is not observed for the S-dmeen complexes, the aziridine complexes, or the pyridine complexes as can be seen by a comparison of the results in Table IV. The quantity Dq^z is evaluated from the equation

$$Dt = {}^4/_7(Dq^{xy} - Dq^z) \qquad (1)$$

Consequently, error in Dq^{xy} resulting from using the octahedral complex value leads to error in Dq^z. Since we have shown that the Dq of a ligand does not remain constant going from complex to complex, Dq^{xy} must be calculated directly from the spectral data of the tetragonal complex.

Table IV

Comparison of the Methods for the Calculation of the Dq of the Axial Ligand[a]

Compound	$Dq(Cl^-)$ I	II	III	Dq^{xy}	$Dq(O_h)$
$Ni(py)_4Cl_2$	680	447	635	1173	985[b]
$Ni(S\text{-}dmeen)_2Cl_2$[a]	591	310	509	1215	1030[c]
$Ni(az)_4Cl_2$	585	347	486	1191	1050[d]
Ni(Temp a)Cl_2	420	...	...	1426	...

[a] All units are cm^{-1}. [b] See ref 10. [c] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4,** 20 (1965). [d] R. T. Kiser and T. W. Lapp, *ibid.*, **1,** 401 (1962).

As can be seen from eq 1, error in the evaluation of Dt also introduces error in Dq^z. The Dt parameters and the corresponding Dq^z in Table IV were evaluated with the inclusion of configuration interaction and the off-diagonal elements which couple the ^3E_g states of the ^3F term. These results are presented in column I.

---

(13) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18,** 88 (1961).

(14) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **2,** 134 (1959).

The results in column III were evaluated by obtaining Dq^{xy} from the spectrum and ignoring all off-diagonal coupling as has previously been done in the literature.[8] The results in column II were obtained employing Dq^{xy} from the octahedral complex and ignoring all off-diagonal coupling. As can be seen, the magnitude of the error introduced by the commonly made approximations is very large. Consequently, we must conclude that it is impossible to obtain meaningful ligand field parameters from electronic spectra that do not contain the requisite number of bands.

The variation of Dq (or Dq') for the axial ligands is of interest. It has been reported that to a good approximation one set of radial parameters will provide constant interpretation of data.[3,15] In Table IV we show that the Dq^z, for chloride ion, calculated by our method (column I), varies dramatically as the Dq^{xy} varies, becoming smaller as Dq^{xy} increases. This conclusively shows that the Dq's of ligands toward Ni(II) are not transferable from complex to complex. This is in direct contrast to the results obtained from the approximate calculations on cobalt(III)[4] and to the assumption later made[16] for a series of cobalt(III) complexes. In view of the results obtained for nickel(II), great caution should be exercised in accepting the conclusions drawn from calculations made assuming the Dq's of ligands are transferable from complex to complex as this is probably not true.

The neglect of off-diagonal coupling also leads to appreciable errors in the crystal field parameter Ds. With the inclusion of configuration interaction *and* the inclusion of the off-diagonal element which couples the ^3E_g states of the ^3F term, we have found that $Ds \approx 2Dt$ in every case studied except for $Ni(S\text{-dmeen})_2(DMF)_2(BF_4)_2$. In this case the ^3E_g and $^3A_{2g}$ components of ^3F ($^3T_{2g}$ in O_h) were not resolved, and the maximum of the transition observed was assumed to be the ^3E_g transition and this may not be a valid assumption. When configuration interaction and the off-diagonal coupling of the $^3E_g(^3F)$ states is neglected, $Ds \approx 1.3Dt$.[9,17]

This error becomes important when we consider the $\delta\sigma$ and $\delta\pi$ parameters of McClure. The quantity $\delta\sigma = \sigma_z - \sigma_{xy}$ where σ_z and σ_{xy} are defined as the σ-antibonding interaction of the ligands on the z and xy axes, respectively. The stronger the σ-donor strength the larger σ. The quantity $\delta\pi$, defined as $\delta\pi = \pi_z - \pi_{xy}$, represents the π-antibonding properties of the ligands on the z and xy axes. The differences in the π-antibonding parameters remove the degeneracies of the t-orbital set. There are two effects contributing to the magnitude of the π parameter that we shall consider here: (1) π-electron repulsion, that is, the repulsion of the lone pairs of ligand electrons with those electrons in the d_{xy}, d_{xz}, and d_{yz} orbitals of the metal; (2) a π-electron back-bonding interaction from filled metal d_{xy}, d_{xz}, and d_{yz} to empty ligand orbitals. The former effect increases the magnitude of π and the latter decreases it.

When configuration interaction is taken into consideration, the sign of $\delta\pi$ is reversed. As an example, consider $Ni(S\text{-dmeen})_2X_2$ where $X^- = Cl^-$ or Br^-. Without configuration interaction, $\delta\pi$ is 156 and 87 cm^{-1}, respectively, whereas with configuration interaction, $\delta\pi$ is -380 and -740 cm^{-1}, respectively. Therefore, when calculating $\delta\pi$, configuration interaction must be considered.

Now let us examine the $\delta\sigma$ parameters. Comparing the values for the S-dmeen complexes and making the assumption that changes in σ_{xy} will be small compared to $\delta\sigma$, we obtain the order for σ_z: DMF > DMSO $\sim$ Cl^- > Br^-. The pyridine complexes produce the order: $Cl^- > Br^- > ClO_4^- > BF_4^-$. The difference in σ-bonding ability between ClO_4^- or BF_4^- and Cl^- or Br^- is not as large as the $\delta\sigma$ numbers because σ_{xy} for pyridine is not constant as indicated by the values of Dq^{yx}. The composite order is: DMF > DMSO $\sim$ $Cl^- > Br^- > ClO_4^- > BF_4^-$. The sign of $\delta\sigma$ indicates the σ values for S-dmeen are greater than for the above ligands. The values of Dq^{xy} indicate Temp a has the largest σ value while py and az are close to those of S-dmeen. In this connection it is worth noting that when py is placed on the z axis in $Ni(py)_2Cl_2$, the sign of $\delta\sigma$ changes.

Since the σ parameters are in the same order as those found in octahedral Ni(II) complexes, this supports previous interpretations from this laboratory of the Dq values of these complexes in terms of σ-donor strengths.[18] The π-antibonding bonding order affects Dq in the opposite direction (*vide infra*), so the differences in Dq are smaller than the differences in σ.

The differences in the $\delta\pi$ numbers are not as large as in $\delta\sigma$. We know from the sign of $\delta\pi$ that the nitrogen donors have larger π values than the anions. We can also obtain the following order from the series in which the xy ligand is held constant, *e.g.*, $Ni(py)_4X_2$ or $Ni(S\text{-dmeen})_2X_2$: DMF > DMSO $\sim$ $Cl^- > Br^- \sim ClO_4^- > BF_4^-$. The constancy of π_{xy} is a good assumption for most of the ions in this series as indicated by the constancy of Dq^{xy} for each series. The position of ClO_4^- is in doubt because Dq^{xy}(py) is quite different from that for the chloro and bromo complexes compared to the difference in $\delta\pi$. It can definitely be placed higher than BF_4^-. This trend is that predicted for decreased coordinating ability of the ligands on the basis of the σ parameter. As the σ-bond strength decreases, the bond lengthens and the antibonding repulsion of the filled lone pair orbitals of the ligand with the metal d_{xy}, d_{xz}, and d_{yz} orbitals decreases. Consequently, the observed π order is attributed to effect (1) above and any metal-to-ligand back-bonding that does occur must not be significant enough to affect the order.

We have been reluctant to make interpretations

---

[15] (a) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964); (b) P Day, *Proc. Chem. Soc.*, 18 (1964).

[16] N. Sadasivan, J. A. Keinolan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).

[17] R. S. Treptow, *ibid.*, **5**, 1593 (1966).

[18] R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1966).

based on differences of 50 cm^{-1} or less. We have reported that Dq varies by 80 cm^{-1} when the value is calculated from mull and solution spectra.[19]

In view of the dominance of σ effects in this series, it is of interest to reexamine the Dq results in Tables III and IV. As the donor properties of the in-plane group increase, as is manifested by our σ order, the metal–chlorine interaction decreases as evidenced by a decrease in Dq^z for chloride. We in effect have a "ligand inductive effect" by the xy ligands decreasing the metal formal charge and decreasing the metal–halogen interaction. Thus the Dq for Cl^- is greater in the pyridine complex than in Ni(Temp a)Cl_2. The values for Dq in the O_h complexes indicate az and S-dmeen interact more strongly with nickel than with pyridine, and in accordance with the ligand inductive effect the Dq of Cl^- is greater in the pyridine complex than in the others. The same trend is observed for the bromo complexes. Consistent with this model we also find that Dq for pyridine is larger in $Ni(py)_4(BF_4)_2$ or $Ni(py)_4(ClO_4)_2$ than in $Ni(py)_4Cl_2$ or $Ni(py)_4Br_2$ as would be expected from the poorer donor strength of BF_4^- or ClO_4^- than of Cl^- or Br^-. Again, we are reluctant to interpret differences in these parameters which are less than 50 cm^{-1} because of lattice effects. Large differences are expected when comparing complexes with one type of in-plane ligands and two axial ligands that are widely different. When four xy ligands are changed and the axial ligands held constant, the differences in ligand donor strengths need not be as large to change Dq^z as the differences need be in the above case ($Ni(L)_4X_2$) when only two ligands are changed.

In conclusion: (1) the Dq of ligands toward nickel does not remain constant as previously thought but often varies in a predictable way with the inductive property of the ligands; (2) when attempting to calculate spectrochemical parameters, all configuration interaction *and* all off-diagonal matrix elements must be considered; and (3) it is impossible to base assignments of spectra on the signs of $\delta\pi$ and $\delta\sigma$, if configuration interaction has not been taken into consideration.

Acknowledgment.—The authors acknowledge the financial support of the research by The National Science Foundation through Grant GP-5498.

[19] In a previous article we incorrectly reported the position of the ${}^3B_{1g} \rightarrow {}^3B_{2g}$ transition of $Ni(py)_4Cl_2$ in solution as being 1400 cm^{-1} different from that in the solid. In solution the bands broaden and are very close. When properly resolved with a Du Pont curve resolver, the difference is only 800 cm^{-1}.

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907

Effect of Steric Hindrance in the 1,1,7,7-Tetraethyldiethylenetriamine Complexes of Copper(II)

By Dale W. Margerum, Barbara L. Powell, and J. A. Luthy

Received October 23, 1967

The proton stability constants of 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) are slightly lower than those of dien with log K values of 9.66, 8.62, and 3.55 for Et_4dien compared to 9.94, 9.13, and 4.34 for dien. On the other hand the stability constant for Cu(II)–Et_4dien (log K_1 = 10.1) is very much less than for Cu(II)–dien (log K_1 = 16.0). The ethyl groups severely hinder coordination of ligands to the out-of-plane positions of copper. The 10^6-fold decrease in the stability constant is attributed primarily to blocking the coordination of water in these axial positions. The log (stability constant) of $[Cu(Et_4dien)OH]^+$ is 6.0 compared to 4.9 for $[Cu(dien)OH]^+$, which is consistent with increased binding of coordinated water in the fourth planar position due to reduced coordination of water in the axial positions. All Et_4dien constants are at 25.0° and 0.1 M ionic strength.

Introduction

Diethylenetriamine (dien) is a well-known ligand which forms quite stable complexes with the transition metals.[1,2] The coordination properties of this tridentate ligand are altered significantly when two ethyl groups are placed on each terminal nitrogen to give 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien).[3] The square-planar complex, $[Pd(Et_4dien)Cl]^+$, has been observed to undergo halide substitution with a kinetic expression similar to that of octahedral complexes.[4,5] It has been called a pseudo-octahedral complex because the ethyl groups, which extend above and below the square-planar configuration, do not permit the normal square-planar substitution mechanism.

Four-, five-, and six-coordinate complexes containing Et_4dien are reported with nickel(II), cobalt(II), and rhodium(III), respectively.[6] Steric crowding of the ethyl groups has been shown to be an important factor in changing the coordination number of nickel

[1] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

[2] H. B. Jonassen, G. G. Hurst, R. B. LeBlanc, and A. W. Meibohm, *J. Phys. Chem.*, **56**, 16 (1952).

[3] Et_4dien also is named and sold as N,N-bis(β-diethylaminoethyl)-amine.

[4] F. Basolo and W. H. Baddley, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

[5] W. H. Baddley and F. Basolo, *ibid.*, **88**, 2944 (1966).

[6] Z. Dori and H. B. Gray, *ibid.*, **88**, 1394 (1966).