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# Spectrochemical Studies of a Series of Lactams as Ligands with Nickel(II) and Chromium(III)

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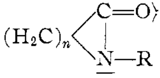
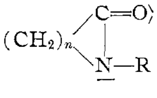
The syntheses and spectra of some nickel(II) perchlorate and chromium(III) perchlorate complexes of a series of lactams of general formula  are described. The ligand field parameters *Dq* and $\beta$ are calculated for the octahedral, oxygen-coordinated complexes. When R is hydrogen and $n = 3$, 4, or 5, the spectrochemical order toward nickel(II) is $5 \sim 4 > 3$. This order is compared to other data on ring size effects. When R is methyl, a steric effect, previously observed for some fully substituted amides,[2] is found to exist between the coordinated lactams. The data obtained in this study confirm many of the conclusions drawn in the study of the amide complexes.

## Introduction

The donor properties of amides of general formula $RC(O)NR_2$ have been extensively studied. Invariably it has been found that oxygen is the principal donor site, and the oxygen is a better donor than is the carbonyl oxygen of acetone. This has been attributed[3] to delocalization of the nonbonding electron pair on the nitrogen into a $\pi$-molecular orbital involving oxygen, carbon, and nitrogen. The inductive effect of the R substituent in the amides is manifested by the following order of donor strengths toward phenol[2]: $HC(O)NHCH_3 \sim CH_3C(O)NH_2 < CH_3C(O)NHCH_3 \sim HC(O)N(CH_3)_2 < HC(O)N(C_2H_5)_2 < CH_3C(O)N(CH_3)_2$.

The preparation and spectral properties of a series of nickel(II) perchlorate and chromium(III) perchlorate complexes of these amides have been reported.[2] The following order indicates the arrangement of these amides in the spectrochemical series: $HC(O)N(CH_3)_2 > HC(O)NHCH_3 \sim HC(O)N(C_2H_5)_2 > CH_3C(O)NH_2 >> CH_3CON(CH_3)_2 > CH_3C(O)NHCH_3$. It was proposed that when both the carbonyl carbon and the nitrogen contained an alkyl substituent, a steric effect exists between coordinated amides causing *Dq* to decrease. This accounts for the division of the above amides into two groups which are separated by a significant amount. The inductive effects of the substituents can be detected within each of the groups.

The series of lactams of general formula



can be studied to provide support for the above interpretations and also to provide information regarding the effect of ring size on the oxygen donor properties of the lactams.

## Experimental

**Preparation.**—The Ni(II) lactam complexes were prepared by the following procedure. The aquated nickel perchlorate was dehydrated with a 100% excess of 2,2-dimethoxypropane (DMP)[4] by stirring for 18 hr. at room temperature. The resulting rust-colored solution then was treated with a 15-fold mole ratio of the lactam which was dissolved in DMP. A large quantity of dry diethyl ether was added, thus precipitating the product. The crystalline product was collected, washed with several portions of dry ether, and dried by pumping at 1 mm. pressure. The unsubstituted lactam complexes formed fine, light green crystals. The N-methyl lactam complexes formed poorly defined, light yellow crystals, which were hygroscopic. The nickel complexes of the N-methyl lactams could only be handled in a drybox.

These abbreviations have been employed for the various lactams: BuL for $\gamma$-butyrolactam ($n = 3$), NMBuL for N-methyl-$\gamma$-butyrolactam, VaL for $\delta$-valerolactam ($n = 4$), NMVal for N-methyl-$\delta$-valerolactam, CaL for $\epsilon$-caprolactam ($n = 5$), and NMCaL for N-methyl-$\epsilon$-caprolactam.

*Anal.* Calcd. for $[Ni(BuL)_6](ClO_4)_2$: C, 37.51; H, 5.51; N, 10.94. Found: C, 37.52; H, 5.62; N, 10.88.

*Anal.* Calcd. for $[Ni(NMBuL)_6](ClO_4)_2$: C, 42.27; H, 6.38; N, 9.8. Found: C, 42.25; H, 6.39; N, 9.84.

*Anal.* Calcd. for $[Ni(VaL)_6](ClO_4)_2$: C, 42.27; H, 6.38; N, 9.82. Found: C, 42.28; H, 6.39; N, 9.56.

*Anal.* Calcd. for $[Ni(NMVal)_6](ClO_4)_2$: C, 46.17; H, 7.10; N, 8.96. Found: C, 46.28; H, 7.26; N, 8.82.

*Anal.* Calcd. for $[Ni(CaL)_6](ClO_4)_2$: C, 46.17; H, 7.10; N, 8.96. Found: C, 46.28; H, 7.21; N, 8.92.

*Anal.* Calcd. for $[Ni(NMCaL)_6](ClO_4)_2$: C, 49.40; H, 7.70; N, 8.23. Found: C, 49.12; H, 7.92; N, 7.91.

The Cr(III) lactam complexes were prepared by the method reported by Madan and Denk for hexakis($\epsilon$-caprolactam)chromium(III) perchlorate, $[Cr(CaL)_6](ClO_4)_3$.[5] The following compounds are reported for the first time:

*Anal.* Calcd. for $[Cr(BuL)_6](ClO_4)_3$: C, 33.30; H, 4.86; N, 9.72; $ClO_4^-$, 34.60. Found: C, 33.42; H, 4.90; N, 9.86; $ClO_4^-$, 34.40.[6]

*Anal.* Calcd. for $[Cr(NMBuL)_6](ClO_4)_3$: C, 38.10; H, 5.73; N, 8.90; $ClO_4^-$, 31.70. Found: C, 38.40; H, 5.79; N, 8.98; $ClO_4^-$, 31.51.

*Anal.* Calcd. for $[Cr(VaL)_6](ClO_4)_3$: C, 38.10; H, 5.73; N, 8.90; $ClO_4^-$, 31.70. Found: C, 38.36; H, 5.91; N, 8.78; $ClO_4^-$, 31.40.

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[1] Postdoctoral National Institutes of Health Fellow, Division of General Medical Sciences, 1963–1964.

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[3] For a summary of the literature see R. L. Middaugh, R. S. Drago, and R. S. Niedzielski, *J. Am. Chem. Soc.*, **86**, 388 (1964).

[4] K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

[5] S. K. Madan and H. H. Denk, *ibid.*, in press.

[6] Perchlorate analyses by nitron reagent: F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand Co., Inc., New York, N. Y., 1947.

**Spectrophotometric Measurements.**—Near-infrared and visible absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. The spectra of the solutions were measured in 1.0-cm. matched quartz cells with the solvent as the reference.

Solutions of the lactam complexes were prepared by dissolving the solid in the respective lactam or, for solid lactams, in a 2.5–4.4 *M* range solution of the lactam in dried spectral grade methylene chloride. Spectral evidence is presented later to indicate that these conditions produce octahedral species in solution.

The O–H frequency shifts for the phenol-N-methyl lactam adducts were obtained by the method previously described.[7] Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer using mulls on sodium chloride plates.

**Calculations.**—A description of the procedure which was followed in making band assignments and calculating ligand field parameters is given in a previous paper.[8]

The electronic spectra for the lactams are similar to those previously reported[2] for the amides. The spectral data are summarized in Table I.

The value for *Dq* and the P–F term splitting for the complexes are given in Table II.

In an attempt to evaluate the magnitude of the interaction of these lactams with phenol, the change in O–H stretching frequency of phenol upon complexation, $\Delta\nu_{O-H}$, was measured. The following values (in cm.$^{-1}$) were obtained: NMBuL, 341 ± 5; NMVaL, 357 ± 6; NMCaL, 350 ± 5. It is not possible to obtain dependable values for $\Delta\nu_{OH}$ for the phenol lactam adducts because of interferences by bands from N–H vibrations. The enthalpy of formation of the phenol-N-methyl lactam adducts listed above are reported[9] to be 6.0, 5.6, and 6.4 kcal. mole$^{-1}$, respectively.

## Discussion

The carbonyl stretching frequency of the lactam is lowered in the complex compared to that in the free ligand. This can be interpreted to indicate oxygen coordination. Elemental analyses and the electronic spectra indicate that the complexes are six-coordinate, octahedral species. The conclusion is substantiated by the constancy of the intensity ratio[2,10,11] of the $^3A_2(F) \rightarrow {}^3T_1(P)$ to $^3A_2(F) \rightarrow {}^3T_1(F)$ absorption bands for the Ni(II) complexes in solution and by the good agreement between the calculated and experimental values for $\lambda_{max}$ of the second band.

The spectrochemical series for these lactam complexes of Ni(II) and Cr(III) shows the predominance of the same type steric effect between ligands that existed in the amides.[2] The *Dq* values for all the N-methyl lactams are significantly lower than those for the unsubstituted compounds. It is interesting that the *Dq* values for the nickel complexes of the N-methyl lactams (780, 759, 749 cm.$^{-1}$) are close to those in the completely alkyl-substituted amide, N,N-dimethylacetamide (769 cm.$^{-1}$), while those for the unsubstituted lactams (810, 833, 834 cm.$^{-1}$) are close to those in the disubstituted amide N,N-dimethylformamide (850 cm.$^{-1}$). It has previously been proposed that the N-methyl group in $CH_3C(O)NHCH_3$ is *cis* to the carbonyl and consequently this amide encounters the same steric effect leading to a lower *Dq* as was observed for N,N-dimethylacetamide in an octahedral nickel(II) complex. In the unsubstituted lactams the methylene group bonded to nitrogen is *trans* to the carbonyl and much higher *Dq* values result. This result serves to confirm the earlier proposal of the existence of a steric effect in the N-methylacetamide complex.

TABLE I

SPECTRAL BANDS FOR Ni(II) AND Cr(III) COMPLEXES OF THE LACTAMS

| Compound | Solvent | $\lambda_{max}$, cm.$^{-1\,c}$ | $\epsilon_{max}{}^a$ | Band assignment[b] |
|---|---|---|---|---|
| $[Ni(BuL)_6](ClO_4)_2$ | BuL | 8,104 | 7.25 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | | 13,350 | 6.69 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 24,630 | 16.3 | $\rightarrow {}^3T_{1g}(P)$ |
| $[Ni(NMBuL)_6](ClO_4)_2$ | NMBuL | 7,800 | 5.61 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | | 12,930 | 5.00 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 24,150 | 14.5 | $\rightarrow {}^5T_{1g}(P)$ |
| $[Ni(VaL)_6](ClO_4)_2$ | 3.0 *M* VaL | 8,327 | 8.60 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | in $CH_2Cl_2$ | 13,350 | 5.94 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 24,600 | 17.7 | $\rightarrow {}^3T_{1g}(P)$ |
| $[Ni(NMVaL)_6](ClO_4)_2$ | NMVaL | 7,587 | 6.81 | $^5A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | | 12,660 | 5.62 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 23,750 | 23.0 | $\rightarrow {}^3T_{1g}(P)$ |
| $[Ni(CaL)_6](ClO_4)_2$ | 4.3 *M* CaL | 8,337 | 9.25 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | in $CH_2Cl_2$ | 13,430 | 5.95 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 24,680 | 18.9 | $\rightarrow {}^3T_{1g}(P)$ |
| $[Ni(NMCaL)_6](ClO_4)_2$ | NMCaL | 7,494 | 7.66 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ |
| | | 13,710 | 5.25 | $\rightarrow {}^3T_{1g}(F)$ |
| | | 23,980 | 19.8 | $\rightarrow {}^3T_{1g}(P)$ |
| $[Cr(BuL)_6](ClO_4)_3$ | BuL | (14,430) | | |
| | | 16,230 | 40.0 | $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ |
| | | 22,940 | 42.8 | $\rightarrow {}^4T_{1g}(F)$ |
| $[Cr(NMBuL)_6](ClO_4)_3$ | NMBuL | (14,370) | ... | |
| | | 15,750 | 52.0 | $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ |
| | | 22,470 | 48.7 | $\rightarrow {}^4T_{1g}(F)$ |
| $[Cr(VaL)_6](ClO_4)_3$ | 2.5 *M* VaL | (14,290) | ... | |
| | in $CH_2Cl_2$ | 16,210 | 54.1 | $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ |
| | | 22,620 | 49.3 | $\rightarrow {}^4T_{1g}(F)$ |
| $[Cr(CaL)_6](ClO_4)_3$ | 4.4 *M* CaL | (14,250) | ... | |
| | in $CH_2Cl_2$ | 16,180 | 58.1 | $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ |
| | | 22,620 | 47.7 | $\rightarrow {}^4T_{1g}(F)$ |

[a] $\epsilon$ is given in l. mole$^{-1}$ cm.$^{-1}$ from the equation $A = \epsilon cl$. [b] The spectra of Ni(II) and Cr(III) complexes of these ligands are very similar to the spectra of the corresponding hexaaquo complexes except for the wave lengths of $\lambda_{max}$. [c] The parentheses designate a low-intensity shoulder on the main peak of the spectrum for the Cr(III) complexes. Shoulders appeared for the Ni(II) complexes of the unsubstituted lactams at a higher frequency than the second band, but were too low in intensity and too broad to be measured accurately. For the Ni(II) complexes the calculated values for $\lambda_{max}$ of the second band agree very well with the experimental values.

TABLE II

SUMMARY OF THE CALCULATED LIGAND FIELD PARAMETERS

| Compound | Solvent | $E(P) - E(F)$ | *Dq*,[a] cm.$^{-1}$ | $\beta^b$ |
|---|---|---|---|---|
| $[Ni(BuL)_6](ClO_4)_2$ | BuL | 13,860 | 810 | 0.88 |
| $[Ni(NMBuL)_6](ClO_4)_2$ | NMBuL | 13,830 | 780 | 0.87 |
| $[Ni(VaL)_6](ClO_4)_2$ | 3.0 *M* VaL in $CH_2Cl_2$ | 13,460 | 833 | 0.85 |
| $[Ni(NMVaL)_6](ClO_4)_2$ | NMVaL | 13,730 | 759 | 0.87 |
| $[Ni(CaL)_6](ClO_4)_2$ | 4.3 *M* CaL in $CH_2Cl_2$ | 13,540 | 834 | 0.85 |
| $[Ni(NMCaL)_6](ClO_4)_2$ | NMCaL | 14,140 | 749 | 0.89 |
| $[Cr(BuL)_6](ClO_4)_3$ | BuL | 10,170 | 1623 | 0.74 |
| $[Cr(NMBuL)_6](ClO_4)_3$ | NMBuL | 10,320 | 1575 | 0.75 |
| $[Cr(VaL)_6](ClO_4)_3$ | 2.5 *M* VaL in $CH_2Cl_2$ | 9,579 | 1621 | 0.70 |
| $[Cr(CaL)_6](ClO_4)_3$ | 4.4 *M* CaL in $CH_2Cl_2$ | 9,484 | 1618 | 0.69 |

[a] The error limits of *Dq* are ±5 cm.$^{-1}$ for Ni(II) and Cr(III) complexes; this error arises in determining $\lambda_{max}$. [b] The error limits of $\beta$ are ±1.2% for Ni(II) and Cr(III) complexes. The quantity $\beta$ is defined as the ratio $B'/B$ where $B'$ is the P–F term splitting for the complex and $B$ the value for the gaseous ion with no crystalline field.

The effect of ring size on the donor strengths of the lactams is not easily assessed. The *Dq* values for the

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nickel(II) complexes of the unsubstituted lactams suggest a donor order based on ring size of 5- $<$ 6- $\sim$ 7-membered. In contrast, in the chromium(III) complexes of the same lactams, no variation of donor strength with ring size is found. A monotonic decrease in donor strength with increasing ring size is indicated by the $Dq$ values for the N-methyl lactam complexes of nickel(II). Here, however, steric factors may be of considerable importance in determining the order.

The phenol frequency shifts for the methyl lactams give a donor order of 5- $<$ 6- $\sim$ 7-membered ring. This is the same order given by the $Dq$ values for the unsubstituted lactam complexes of nickel(II).

The $\Delta H$ values for 1:1 complex formation between the methyl lactams and phenol, measured by ultraviolet spectrophotometry, give still a different order.[9] Finally, the p$K_a$ values for the unsubstituted lactams indicate an order of basicity of 5- $<$ 7- $<$ 6-membered ring, which is similar to that shown by the $Dq$ values for the nickel(II) complexes.[12]

Studies on the effect of ring size on the basicity of other cyclic carbonyl compounds such as saturated cyclic ketones[13,14] and lactones[15] indicated an increasing basicity with increasing ring size. The generally observed decreased basicity of the smaller (4- and 5-membered) ring compounds relative to the larger ones has been rationalized.[12,15] In general, it is found that the carbonyl stretching vibration occurs at higher frequencies for smaller ring compounds than for the larger ones. For example, the carbonyl bands for cyclobutanone, cyclopentanone, cyclohexanone, and cycloheptanone are at 1775, 1751, 1718, and 1706 cm.$^{-1}$, respectively.[16] The lactams show a similar decrease in the carbonyl stretching frequencies in going from the 4-membered to the 6-membered ring.[15] In the lactam case, the carbonyl stretching frequencies for BuL, VaL, and CaL are 1691, 1651, and 1560 cm.$^{-1}$, respectively.[17]

The $Dq$ values for the nickel(II) complexes of the unsubstituted lactams correlate with the carbonyl stretching frequencies. However, the $Dq$ values for the chromium(III) complexes do not, nor do the $Dq$ values obtained for the methyl lactam complexes of nickel(II). From the data presented in this paper, it would appear that several varying factors are operative in determining the donor order of these lactams and a definitive statement regarding the effect of ring size cannot be made.

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# Octahedral Nickel(II) Complexes of Secondary and Tertiary N-Alkylethylenediamines[1]

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A series of tris complexes of nickel(II) perchlorate and several N-alkyl-substituted ethylenediamines has been isolated from nonaqueous solutions and characterized. The spectral and magnetic data indicate that the complexes possess octahedral structures. The first d–d transition (${}^3A_{2g} \rightarrow {}^3T_{2g}$) of the complexes, in the solids and in their respective ligands as solvents, shifts systematically to lower energy values as the alkyl group on the ethylenediamine ligand becomes more complex. The resulting spectrochemical series is: en $>$ N-methylen $>$ N-ethylen $>$ N-propylen $>$ N,N′-dimethylen $>$ N-methyl-N′-ethylen $>$ N,N-dimethylen, where en = ethylenediamine. The smaller $Dq$ values which result with increasing alkyl substitution demonstrate that steric interactions are of greater magnitude than the increased inductivity of the substituted ethylenediamines and of more importance in determining the coordination interaction with the Ni(II) ion.

## Introduction

Thermodynamic data on the relative base strengths of alkylamines are based mainly on measurements of acid–base equilibria in water and related hydroxylic solvents. However, Pearson and Vogelsong[2,3] and Trotman-Dickenson[4] have shown that these equilibria are affected by solvation terms, ion-pair association, and entropy effects. The net result of these interactions in the series of alkylamines produces the following general sequence of basicity in water: $R_2NH > RNH_2 > R_3N > NH_3$.

Bjerrum[5] has tabulated the data of several investigators in such a manner as to emphasize the rather good

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(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

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