

solid state the nitrates are coordinated to the copper(II) ion. This result can only mean that DMF solvent molecules are able to displace the nitrate ligands. Such is not the case for the chloride complexes. While the molar conductances of these latter vary from 7.0 for $\text{Zn}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2$ to 42.9 for $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2 \cdot \text{H}_2\text{O}$, it is obvious that some chloride coordination persists even at the dilutions used for the conductivity measurements. Rather obviously, the bromide ion is easily displaced by solvent from $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Br}_2 \cdot \text{H}_2\text{O}$.

The magnetic moments, each calculated from replicate measurements at one temperature (25°), fall well within the range of values usually obtained

for the ions concerned, except in the case of $\text{Cu}(\text{II})$. The values tabulated for $\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2$ and $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2$ are obviously low, indicative of insufficient magnetic dilution of individual ions. The values for the other two copper(II) complexes are normal.

Our reluctance to use brackets, [], to indicate structural entity for seven of the metal complexes listed in Table I merely indicates that we retain considerable doubt as to several possible, reasonable structures based upon the colors, magnetic properties and solute behavior.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

Transition Metal Complexes of Pyridine N-Oxide

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The preparation and characterization of several complexes containing pyridine N-oxide as a ligand are reported. In each case, the metal ion attains its maximum coordination number. The chemical effects of a charge transfer band in these complexes near the visible range are discussed.

The affinity of pyridine N-oxide for protons has been demonstrated. The equilibrium constant for proton donation by the conjugate acid in aqueous solution has been measured,¹ yielding a pK_a of 0.79, and the determination² of the crystal structure of the hydrochloride and hydrobromide of pyridine N-oxide indicates the presence of the $\text{C}_5\text{H}_5\text{NOH}^+$ ion.

Recent interest in the donor properties of covalent molecular oxides has led us to extend these studies of the basicity of pyridine N-oxide by investigating its reactions with transition metal ions. We mention specifically the related work of Cotton and Bannister³ on complexes of transition metal ions with triphenylphosphine oxide, as well as the similar complexes which have been prepared^{4,5} containing dimethyl sulfoxide as a ligand. An indication of the basicity of pyridine N-oxide, relative to these molecules acting as donors, may be obtained by a comparison of the dipole moments of the three molecules: 4.24 D. for pyridine N-oxide⁶ and 4.28 and 3.9 D., respectively, for triphenylphosphine oxide⁷ and dimethyl sulfoxide.⁴ In each case, since the oxygen atom is the negative end of the dipole, one would expect facile formation of complexes with transition metal ions. It has been shown that $(\text{C}_6\text{H}_5)_3\text{PO}$ bonds to metal ions through the oxygen atom⁸ but that $(\text{CH}_3)_2\text{SO}$,

although it usually forms an M-O bond, occasionally bonds through the sulfur atom as well.⁹ In the present instance, we would expect pyridine N-oxide to coordinate only through the oxygen atom.

Previous investigations involving donation by amine oxides are limited to studies¹⁰ on the reaction of trimethylamine oxide with several Lewis acids (BF_3 , SiCl_4) and some recent studies¹¹ on the complexes of adenine and adenosine 1-N-oxides with metal ions.

Experimental¹²

Reagents.—Pyridine N-oxide was obtained commercially and purified by vacuum sublimation. All the salts and solvents used in the preparation of complexes were of reagent grade.

Visible spectra were obtained with a Beckman Model DK-1 recording spectrophotometer.

Preparation of the Complexes.—All compounds reported here were prepared simply by adding a warm methanolic solution of pyridine N-oxide to a similar solution of the appropriate hydrated metal perchlorate. In each case, crystals of the complex precipitated on cooling. The compounds prepared to date are listed in Table I. The formation of the complex of chromium(III) was hastened by boiling the solution for a short time. Note the preparation of two different complexes of the cupric ion; these were prepared simply by varying the stoichiometry of the reactants. All of the complexes were dried *in vacuo* at 60°. They are readily soluble in acetonitrile. Visible spectra are summarized in Table II.

Discussion

Work thus far has been limited to the complexes formed by metal perchlorates; this has simplified

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- (3) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873 (1960); E. Bannister and F. A. Cotton, *ibid.*, 1878 (1960).
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- (5) D. W. Meek, D. K. Straub and R. S. Drago, *ibid.*, **82**, 6013 (1960).
- (6) E. P. Linton, *ibid.*, **62**, 1945 (1940).
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- (12) All analyses are by Dr. S. M. Nagy of the Massachusetts Institute of Technology. Some difficulty was encountered in the analyses of several of the reported compounds because of their explosive nature.

TABLE I
 COMPLEXES OF PYRIDINE N-OXIDE WITH METAL PERCHLORATES

Compound	Color	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %		Metal, %	
		Theor.	Found	Theor.	Found	Theor.	Found	Theor.	Found	Theor.	Found
$[\text{Cr}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	Emerald green	39.12	38.79	3.26	3.14	9.12	9.30			5.65	5.45
$[\text{Mn}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	Yellow	43.66	44.45	3.64	3.63	10.19	10.64			6.66	6.22
$[\text{Fe}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2 \cdot \text{C}_5\text{H}_5\text{NO}$	Yellow	41.21	40.87	3.43	3.25	9.61	9.38			5.48	5.52
$[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	Brick red	43.49	43.53	3.62	3.33	10.14	10.65			7.11	6.41
$[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	Yellow-green	43.46	43.40	3.62	3.29	10.14	10.28			7.08	7.08
$[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4](\text{ClO}_4)_2$	Green-blue	37.36	37.56	3.11	2.37	8.71	8.74	11.04	10.78	9.88	8.95
$[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	Yellow-green	43.25	43.00	3.60	3.44	10.08	10.03	8.52	8.61	7.63	7.56
$[\text{Zn}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	White	43.11	43.15	3.59	3.81	10.06	10.26			7.83	7.61
$[\text{Hg}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	White	37.14	37.58	3.09	2.92	8.66	8.96	7.32	7.41		

 TABLE II
 VISIBLE SPECTRA OF THE COMPLEXES IN ACETONITRILE

Complex ion	Band maxima, Å.	Onset of charge transfer, Å.
$[\text{Cr}(\text{C}_5\text{H}_5\text{NO})_6]^{3+}$	6500, 4485	3875
$[\text{Mn}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$	3834	4500
$[\text{Fe}(\text{C}_5\text{H}_5\text{NO})_6]^{3+}$	5000
$[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$	5000, 3714	4300
$[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$	11,000, 6305, 3785	4300
$[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4]^{2+}$	7420	4000
$[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$	7390	4300

the problem of the characterization of the complexes. Based on our knowledge of the aquo complexes of these metals as well as those molecules containing $(\text{C}_6\text{H}_5)_3\text{PO}$ and $(\text{CH}_3)_2\text{SO}$ as ligands, there is little that is unusual in our formulation of these compounds. We note several interesting features, however, such as the fact that the metal ions tend to attain their maximum coordination number toward pyridine N-oxide as a ligand as well as the yellow cast or color that is present in many of the compounds. The extreme ease with which all of these complexes form should be noted. The complexes are decomposed rapidly when placed in water. Pyridine N-oxide is very hygroscopic but only the manganese complex is affected by standing in air.

The reaction of manganous perchlorate with pyridine N-oxide yielded a bright yellow compound. In view of the usual pink color of manganous ion when attached to simple oxygen donors, we were at first surprised by the strong coloration. The question arose as to whether the complex was of the expected type, containing manganous ion in a $^6\text{A}_1$ state, but also with a charge transfer band at unusually low energy which trailed off into the visible. The paramagnetic susceptibility of the compound was kindly measured for the author by Dr. A. P. Ginsberg of the Bell Telephone Laboratories. The measurement, at room temperature with a Faraday-type balance, yielded an effective magnetic moment of 5.88 B.M., quite consistent with a sextet ground state for the metal ion. The yellow color is caused by a strong charge transfer band at about $380\text{ m}\mu$ which trails into the visible; no d-d electronic transitions were found in the spectrum. Similar strong charge transfer interaction, as noted in Table II, causes the very bright yellow color of the ferric compound, as well as the yellow cast of several of the other compounds we report. This intense interaction of charge transfer was unexpected with the pyridine N-oxide complexes as no such interference with the normal

color of metal ions was reported in the complexes of triphenylphosphine oxide and dimethyl sulfoxide.

Transition metal complexes with charge transfer bands very close to the visible region appear to decompose readily. In the present case, the manganese compound slowly turns greenish-black in air. A strong odor of pyridine persists over the compound. This decomposition appears to be due, not to attack by water, but to attack by either light or oxygen. Similar instability has been noted with ferric acetylacetonate, a compound where the charge transfer band extends far into the visible.¹³ Single crystals of this material crumble after standing in air.

Perhaps the greatest difference between pyridine N-oxide and the two ligands we are comparing it with, triphenylphosphine oxide and dimethyl sulfoxide, is the steric one. Six molecules of either $\text{C}_6\text{H}_5\text{NO}$ or $(\text{CH}_3)_2\text{SO}$, each donating through the oxygen atom, would be expected to have little difficulty in arranging themselves in octahedral coordination about the central metal ion. Such is not the case with $(\text{C}_6\text{H}_5)_3\text{PO}$, each molecule of which sweeps out a large amount of space. This observation is substantiated by the absence of any report of a complex of $(\text{C}_6\text{H}_5)_3\text{PO}$ with coordination number greater than four. Pyridine N-oxide and dimethyl sulfoxide each cause the metal ion to attain a coordination number of six. Interesting in this respect is the preparation of both $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4](\text{ClO}_4)_2$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$. It is unusual for copper to form a six-coordinate complex with the ease here reported. The complex with four ligands is readily transformed to the one with six ligands by treatment with excess pyridine N-oxide. Pale blue $[(\text{C}_6\text{H}_5)_3\text{PO}]_4\text{Cu}(\text{ClO}_4)_2$ has been reported⁸ to absorb at $700\text{ m}\mu$, and we find both of our copper complexes absorbing in the same region but at slightly lower energy. Again, the great difference in colors is due to the onset of strong charge transfer interaction.

The chromium and cobalt complexes are quite as expected, in color and stoichiometry, and the charge transfer does not interfere very seriously with the visible spectrum. The nickel compound is unusual in its yellow cast, but this is readily explained by the observation of the charge transfer tail in the visible region. Noteworthy in this respect are the pure white colors of the zinc and mercuric complexes.

It has been reported⁴ that dimethyl sulfoxide

(13) R. L. Carlin, Thesis, University of Illinois, 1960.

yields no well-defined complexes with mercuric halides, and Drago⁵ reported the preparation of $\text{Hg}(\text{SCN})_2 \cdot 2(\text{CH}_3)_2\text{SO}$, a compound of undefined structure. No mercuric complex of $(\text{C}_6\text{H}_5)_3\text{PO}$ has been reported. Our preparation, then, of $[\text{Hg}(\text{C}_6\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ is the first example of a well-defined mercuric complex of this type. Again, the attainment of a maximum coordination number should be noted.

An investigation of the reaction of pyridine N-oxide with other salts of these metals is in progress. We mention in particular the preparation of compounds which appear to have the formula $\text{M}(\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$, $\text{M} = \text{Cu}, \text{Ni}$. These compounds, which will be reported on in detail later, probably can be formulated as $[\text{M}(\text{C}_6\text{H}_5\text{NO})_2(\text{NO}_3)_2]$, with coordination by nitrate, as was found for the triphenylphosphine oxide complexes of metal nitrates.¹⁴

(14) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

The intense charge transfer interaction that has been noted above appears to have been overlooked in the literature, for there is indeed a large number of strongly colored complexes whose color is due to this process. In order to examine this situation more closely, two paths of research are indicated. The complexes reported here contain central ions which have either a filled or an unfilled d shell; only the complexes of the latter type exhibit charge transfer bands close to the visible. Current work is directed toward preparing a larger selection of complexes with both types of metal ions, with the expectation that a correlation of strong charge transfer bands in complexes of metal ions with incomplete electronic shells will prevail. The other path being investigated concerns the complexes of alkylamine N-oxides. It is expected that the different environment of the nitrogen atom in these molecules will also affect the charge transfer process.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Molecular Association and Electronic Structures of Nickel(II) Chelates. II. Bis-(3-Phenyl-2,4-pentanediono)-nickel(II) and High Temperature Studies of Nickel Acetylacetonate

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Additional support is given to the premise that association of molecules with one another must be considered in attempting to explain the spectral and magnetic behavior of Ni(II) complexes. Visible absorption spectra of bis-(2,6-dimethyl-3,5-heptanediono)-Ni(II), bis-(2,4-pentanediono)-Ni(II) and bis-(3-phenyl-2,4-pentanediono)-Ni(II) at 80, 120, 160 and 200° in diphenylmethane are described in terms of an equilibrium between monomers and polymers. The temperature and concentration dependent spectrum of bis-(3-phenyl-2,4-pentanediono)-Ni(II) in toluene has been analyzed in terms of monomer-trimer equilibria from 0–50°. Anhydrous bis-(3-phenyl-2,4-pentanediono)-Ni(II) and bis-(dibenzoylmethano)-Ni(II) have been isolated as solids in two forms, a green paramagnetic material (presumably polymerized) and a red diamagnetic material.

Introduction

X-Ray work² has established that crystalline anhydrous bis-(2,4-pentanediono)-nickel(II) ($\text{Ni}(\text{AA})_2$) contains trimeric molecules in which some of the pentanediono oxygen atoms serve as bridges between nickel ions in such a way that the nickel ions all become octahedrally coordinated. Molecular weight measurements are in accord with the view that these trimeric units are preserved when the compound is dissolved in non-coordinating solvents³ at room temperature and as high as at least 80° and the ultraviolet spectra of such solutions can best be understood using this assumption.⁴ It has also been shown⁴ that when the methyl groups in $\text{Ni}(\text{AA})_2$ are replaced by *t*-butyl groups, to give bis-(dipivaloylmethano)-nickel(II), $\text{Ni}(\text{DPM})_2$, steric hindrance completely prevents trimerization and the complex behaves as a spin-paired planar nickel(II) complex, whereas,

when the methyl groups are replaced by isopropyl groups, giving bis-(diisobutyrylmethano)-nickel(II) ($\text{Ni}(\text{DIBM})_2$), the complex exhibits partial, reversible and temperature-dependent association between 0 and 60°.

In this paper, we describe studies of the association equilibrium of $\text{Ni}(\text{DIBM})_2$ at temperatures above 60°, from which the molar extinction of the visible band characteristic of the monomer is obtained, studies of $\text{Ni}(\text{AA})_2$ at temperatures up to 200°, which show that the trimer of this complex also dissociates reversibly into monomers at sufficiently high temperatures, and finally studies of the reversible association of bis-(3-phenyl-2,4-pentanediono)-nickel(II)-($\text{Ni}(\text{PPD})_2$).

Experimental

The high temperature spectra were run using a Cary Model 14 spectrophotometer equipped with a special heated cell housing designed at the Argonne National Laboratory for spectral study of molten salt solutions. Our use of this instrument, at the Argonne Laboratory, was made possible by the generosity and assistance of Dr. D. M. Gruen and Mr. R. L. McBeth. The temperatures reported in this work are believed to be reliable to within $\pm 1^\circ$. Spectra were recorded from 400 to 1500 $\text{m}\mu$; the solvents have a

(1) Alfred P. Sloan Foundation Fellow.

(2) G. J. Bullen, R. Mason and P. Pauling, *Nature*, **189**, 291 (1961).

(3) R. Soderberg, unpublished work. Ebullioscopic measurements in benzene and carbon tetrachloride give association factors of, respectively, 2.96 ± 0.2 and 2.90 ± 0.1 .

(4) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).