is summarized by eq 3 in terms of the oxidation states

$$\mathrm{Pb^{II}OEP} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{II}OEP^+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{IV}OEP} \qquad (3)$$

of porphyrin and Pb. That loss of the second electron gives Pb^{4+} bound to unoxidized porphyrin is at first glance surprising. However, it is reasonable in terms of the expected instability of a Pb(III) complex and it is consistent with the known tendency of lead to undergo net two-electron transfer.

The formation of a stable, covalent metalloporphyrin *via* reduction of a labile, easily formed ionic complex is noteworthy. This heretofore unobserved

$$\mathrm{Pb^{IV}OEP} \xrightarrow{+2e^-} \mathrm{PbOEP}$$

type of reaction may have important consequences both in the laboratory and biosynthesis of metalloporphyrins.

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Uni- and Bimetallic Complexes Derived from a Substituted Pyrazine Ligand

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An attempt has been made to synthesize a substituted pyrazine molecule that would be capable of complexing simultaneously with two metal ions such that there exists an isolated bimetallic species. Of the Co^{2+}, Ni^{2+}, and Cu^{2+} complexes prepared, only the copper complex formed a compound with the desired stoichiometry. Low-temperature magnetic data indicated little metal–metal interaction in the system. It is believed that both nitrogens of the pyrazine are not involved in coordination in the bimetallic species.

Introduction

The purpose of synthesizing and studying this series of compounds was to investigate the possibility of there being metal–metal interaction between two isolated metal centers when bridged by pyrazine. With this type of ligand it was hoped to obtain the coordination shown in Figure 1. Some of the early work[1,2] with pyrazine was concerned with its ability to utilize both of its nitrogen atoms as donors and form polymers. This work came into sharp focus in a series of papers by Lever, Lewis, and Nyholm[3–6] dealing with the Co^{2+}, Ni^{2+}, and Cu^{+} complexes of pyrazine. They were able to demonstrate the ability of pyrazine and its methyl-substituted derivatives to form monomeric, dimeric, and polymeric species. Recently there has been evidence that pyrazine can act as a bridging ligand such that there is spin–spin interaction between the metal centers.[7–9] Since most of the previous work with pyrazine–metal complexes had dealt with polymeric systems, it was thought desirable to synthesize a substituted pyrazine ligand such that the substituents would wrap around two metal ions and form a bimetallic system bridged by the pyrazine moiety. Cotton and Gibson's[9] epr work suggested that metal–metal interaction in a bimetallic species might be present. It has also been demonstrated that there is enhanced basicity of the second nitrogen in pyrazine when complexed with pentaammineruthenium(II)[10,11] and that there was interaction between the two ruthenium ions in the pentaamminepyrazineruthenium mixed oxidation state species reported by Creutz and Taube.[12] These papers suggest a pathway through the aromatic base for metal–metal interaction.

Attempts to synthesize substituted pyrazines and study their transition metal chemistry have resulted in compounds analogous to 2,3,5,6-tetrakis(α-pyridyl)pyrazine[13–15] which show only the ability to be tridentate and not bis tridentate. This paper describes the synthesis of bis(*N*-2-(2-ethylpyridyl))-2,3-pyrazinedicarboxamide (Figure 1) using as a starting material 2,3-pyrazinedicarboxylic acid. Of the transition metal complexes prepared with the new ligand, only the copper(II) compound was bimetallic. It is believed that both nitrogens of the pyrazine ring are not involved in coordination in the bimetallic species.

Experimental Section

Preparation of Ligand.—2,3-Pyrazinedicarboxylic acid from Aldrich Chemical Co. was the starting material. The dimethyl ester was prepared by refluxing 50 g of the diacid in 500 ml of methanol with 7 ml of H_2SO_4 for at least 15 hr. The methanol was evaporated to 250 ml and 1 l. of water was then added. The solution was neutralized over $NaHCO_3$ and extracted six times with 250 ml of ether. The ether was dried over Na_2SO_4. A yellowish oil remained when the ether was evaporated which yielded white crystals when placed in the refrigerator. The yield was 82%. The product was recrystallized from ether, mp 50–51°.

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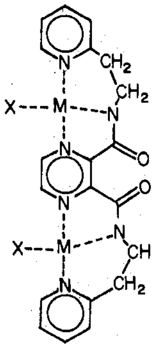

Figure 1.—Desired bimetallic complex of bis(*N*-2-(2-ethylpyridyl))-2,3-pyrazinedicarboxamide. It is believed this configuration was not obtained.

The nmr taken in $CDCl_3$ showed two peaks: CH_3 at τ 5.95 and the aromatic protons at τ 1.2.

Bis(*N*-2-(2-ethylpyridyl))-2,3-pyrazinedicarboxamide was prepared by refluxing the dimethyl ester with 2-(2-aminoethyl)-pyridine in methanol such that there was a 1:2 stoichiometric ratio. After refluxing for 24 hr the methanol was evaporated on the Roto-Vap leaving a light yellow oil which crystallized after placing it in the refrigerator. The material was recrystallized from benzene–tetrahydrofuran (4:1) to yield white crystals, mp 136–137°. Nmr spectrum ($CDCl_3$): τ 7.87 (triplet, CH_2 adjacent to pyridine), 6.15 (quartet, CH_2 adjacent to NH), 3.13–2.13 (complex, aromatics of pyridine), 2.16 (broad, NH of amide), 1.66 (doublet, aromatic protons in ortho position of pyridine), 1.60 (sharp singlet, aromatic protons of pyrazine). Ir spectrum (Nujol, cm^{-1}): 3280 (b), 2330 (w), 1640 (b), 1585 (m), (1555, 1530, 1520 (b)), (1460, 1445, 1425 (b)), 1360 (m), 1350 (m), 1310 (m), 1290 (m), 1270 (m), 1210 (w), 1185 (s), 1145 (s), 1110 (s), 1068 (w), 1045 (s), 1015 (m), 1000 (s), 982 (s), 880 (s), 860 (m), 850 (m), 830 (w), 765 (s), 755 (w), 740 (w), 640 (b). *Anal.* Calcd for $C_{20}H_{20}N_6O_2$: C, 63.82; H, 5.37; N, 22.33. Found: C, 63.85; H, 5.60; N, 22.06.

Preparation of Complexes.—A solvent diffusion method was used to prepare the Cu^{2+} and Ni^{2+} complexes with the ligand. A small amount of the ligand was dissolved in methanol and placed in a small vial. This small vial was then placed in a larger vial containing methanol such that the smaller vial was completely immersed. A disposable pipet was then used to layer on the bottom of the larger vial a saturated solution of the metal salt in methanol. The larger vial was then sealed. After a few days crystals formed at the lip of the smaller vial. This method was employed using $CuCl_2$, $Cu(NO_3)_2$, and $Ni(ClO_4)_2$. Analyses for C, H, N, and Cl were done by Chemalytics of Tempe, Ariz. Copper analysis was accomplished *via* neutron activation analysis at the University of California, Irvine, Calif. After analysis, the results indicated the following stoichiometries: Cu_2LCl_3, $Cu_2L(NO_3)_3$, and $NiL(ClO_4)_2 \cdot 2MeOH$. *Anal.* Calcd for Cu_2LCl_3: C, 39.45; H, 3.15; N, 13.80; Cl, 17.47; Cu, 20.87. Found: C, 39.21; H, 3.11; N, 13.94; Cl, 16.76; Cu, 21.52. Calcd for $Cu_2L(NO_3)_3$: C, 34.89; H, 2.78; N, 18.30. Found: C, 35.00; H, 2.67; N, 18.25. Calcd for $NiL(ClO_4)_2 \cdot 2MeOH$: C, 37.85; H, 3.18; N, 12.04; Cl, 10.16. Found: C, 37.02; H, 3.20; N, 12.12; Cl, 9.50.

The cobalt complex with the ligand was prepared by dissolving a large excess of $Co(ClO_4)_2 \cdot 6H_2O$ in water and then adding a small amount of the ligand dissolved in water. After standing 1 week with the flask open to the air, beautiful brown needles formed that analyzed as $CoLClO_4$. Anal. Calcd for $CoLClO_4$: C, 45.08; H, 3.41; N, 15.77; Cl, 6.65. Found: C, 45.41; H, 3.98; N, 15.67; Cl, 5.47.

Magnetic Susceptibility Measurements.—Susceptibility measurements were made from approximately 4.5 to 383°K. Faraday measurements were made down to 80°K using an Alpha/Ainsworth Model 1071 electronic balance and the Alpha Model 1424 variable-temperature accessory system. A Princeton Applied Research FM-1 vibrating sample magnetometer, coupled with an Andonian Associates liquid helium dewar, was used for the temperature measurements below liquid nitrogen temperature.

All susceptibility measurements were done on solid samples. The temperature measurements in the magnetometer were made potentiometrically with a Ga–As diode that had been calibrated against an NBS Ga–As diode. The magnetometer measurements are relative susceptibilities which were converted to cgs units by comparing them to the Faraday measurements at overlapping temperatures. The standard used for the Faraday measurements was $Hg(Co(SCN)_4)$. All susceptibilities have been corrected for the diamagnetism of the ligands, metals, and sample container. The diamagnetism of the organic ligands was measured directly. The diamagnetism values for the metals and inorganic ligands were taken as given by Pascal.[16] The susceptibilities have been corrected for temperature-independent paramagnetism (TIP) using a value of 60×10^{-6} cgsu[17] for copper and a value of 240×10^{-6} cgsu[18] for nickel. The precision of the copper magnetic moments was 0.05 BM for the Faraday measurements. The precision of the nickel complex was 0.02 BM. On the basis of the $Hg(Co(SCN)_4)$ standard comparisons the accuracy of the Faraday susceptibility measurement was *ca.* 2%. The accuracy of the magnetometer measurement was estimated as being better than 5%.

Spectral Measurements.—The visible spectra were recorded on a Cary 14 spectrophotometer by making KBr pellets of the samples. It was possible to measure the solution spectrum of the cobalt complex due to its solubility in water.

Results

A Curie–Weiss equation was calculated for all three compounds using all the data, *viz.*

$$\chi_M{}^{Ni} = \frac{1.35}{T + 4.16} + 240 \times 10^{-6} \text{ cgsu}$$

$$\chi_M{}^{Cu}(\text{chloride}) = \frac{0.405}{T - 4.42} + 60 \times 10^{-6} \text{ cgsu}$$

$$\chi_M{}^{Cu}(\text{nitrate}) = \frac{0.418}{T + 0.33} + 60 \times 10^{-6} \text{ cgsu}$$

A conventional least-squares analysis was performed to obtain the equations. The independent variable was $1/\chi_M$ where χ_M had been corrected for TIP as well as all diamagnetic effects as mentioned previously. Using the slope of each of the above equations yields the following magnetic moments for the three compounds: $\mu_{eff}{}^{Ni} = 3.29\ (\pm 0.07)$ BM; $\mu_{eff}{}^{Cu}(\text{chloride}) = 1.80\ (\pm 0.04)$ BM; $\mu_{eff}{}^{Cu}(\text{nitrate}) = 1.82\ (\pm 0.04)$ BM. μ was calculated per mole of copper present in the complex. This, of course, carries the implication that half of the molecular weights of Cu_2LCl_3 and $Cu_2L(NO_3)_3$ were used in the respective calculations of χ_M.

The beige nickel complex showed no spectral transitions that could be attributed to "d–d" transitions due to a charge-transfer peak trailing into and throughout the visible region. The same charge-transfer mechanism was manifest in the cobalt and copper spectra but did not completely obscure some of the "d–d" transitions. The solution spectrum, as well as the solid-state spectrum of the cobalt complex, was quite similar, showing a maximum at 525 mμ. The solid-state spectrum of the copper complexes showed a very broad manifold starting at 550 mμ and extending into the near-infrared region to approximately 1600 mμ. The maximum is centered at 790 mμ.

Discussion

One of the surprising aspects of this series of compounds occurred in the two copper complexes. Even

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(17) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 263.

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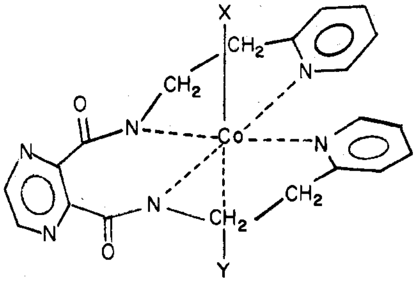

Figure 2.—Postulated coordination of $CoLClO_4$. Octahedral coordination could be completed by water molecules or carbonyl groups from adjacent molecules in the crystal lattice.

though the nitrate and the chloride salts are bimetallic in that the stoichiometry of copper to ligand is 2:1, the metal sites are evidently well isolated from each other. This follows from the observation that the susceptibility obeys very closely a Curie–Weiss law, and the magetic moment is essentially constant with the exception of the last data point in the vicinity of 4.5°K (1.66 and 1.71 BM for the nitrate and chloride, respectively).

Another surprising aspect was the magnetic moment of the beige Ni complex. From the color one would expect square-planar coordination and hence no unpaired electrons.

Still another interesting feature occurred when the magnetic susceptibility of the cobalt complex was measured and found to be diamagnetic.

The cobalt was oxidized to the 3+ oxidation state and as a result is low-spin d^6. In order for the stoichiometry to be satisfied this means that both of the amide protons must be ionized. Figure 2 shows the type of coordination that must be present as a consequence. The vast majority of Co^{3+} complexes are octahedrally coordinated with a transition in the visible region ($A_{1g} \rightarrow T_{1g}$) occurring at *ca.* 500 mμ. The cobalt spectrum is commensurate with octahedral coordination (one cannot argue cis or trans due to the charge-transfer mechanism). Since the perchlorate band is not split in the infrared region (1070 cm^{-1}), one must postulate that the octahedral coordination is completed in some other fashion. Remembering that the solution spectrum is similar to the spectrum taken with the KBr pellet, it is not unreasonable to postulate that oxygen atoms from water occupy the axial positions in solution, whereas oxygen atoms from the carboxyl groups of adjacent molecules occupy the axial positions in the solid state.

Based on the magnetic moment of the nickel complex it is reasonable to assume that the nickel ion is in an approximately octahedral environment similar to the cobalt. Since octahedral nickel has an A_{2g} ground state, one would expect there to be less of an orbital angular momentum contribution to the magnetic moment than for the case of the tetrahedral, T_{1g} ground state. As a result of octahedral coordination nickel complexes have moments between 2.83 and 3.4 BM. The value of 3.29 BM for the diamide complex is seen to be in the expected range for octahedral coordination. As with the cobalt complex the perchlorate band in the infrared region (1080 cm^{-1}) is not split for the nickel complex. This does not contradict the suggestion that the coordination is similar for the two complexes.

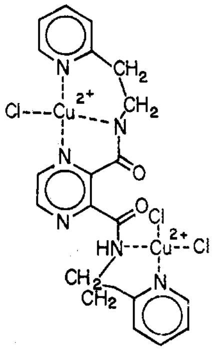

Figure 3.—Postulated coordination of bimetallic copper complexes.

One other feature is noticeable about the magnetic measurements of the nickel complex. The magnetic moment ($\mu_{eff} = 2.828\sqrt{\chi_M T}$) is not constant over the temperature range. μ_{eff} falls from 3.24 to 2.39 BM from 92.8 to 4.42°K. The decrease in μ_{eff} is indicative of antiferromagnetism and could arise *via* an indirect pathway. Such weak interactions have been reported in other nickel complexes. Robinson and Friedberg[19] have measured the specific heats of $NiCl_2 \cdot 6H_2O$ over the temperature range of 1.4–20°K, and their measurements indicate that $NiCl_2 \cdot 6H_2O$ transforms into an ordered state below 5.34°K which they suggest is antiferromagnetic. It is suggested in their paper that the Cl^- ions could provide paths for indirect exchange coupling of the nickel moments. The coupling is very weak for the nickel complex reported here as can be seen from a plot of χ *vs.* T.

The postulated coordination of the dimeric copper complexes is as shown in Figure 3. If each nitrogen atom on the pyrazine ring were coordinated to a copper atom, one might expect that there would be coupling of the electrons through the π aromatic system similar to that found by Hatfield.[7] If there is interaction between the metal centers in the bimetallic species, it is very small and is just beginning to become obvious at the last data point for both the chloride and nitrate. There is some deviation from the Curie–Weiss equation presented that becomes apparent at low temperatures (below 11°K) for the Cu_2LCl_3 complex which is more manifest than for the other copper complex. However, as indicated by the magnetic moment calculations the effect is not as severe as one observes from a comparison of calculated *vs.* observed molar susceptibilities. Rather the difference in the calculated and observed susceptibilities arises partially as a result of the error in the Weiss constants (±1.0°). One is therefore forced to conclude that the metal centers are magnetically quite isolated from each other. The type of coordination in Figure 3 fulfills the stoichiometric requirements provided one of the amide protons is ionized. The very broad absorption band for the copper complexes is rationalized by the fact that each of the two copper atoms must be in different environments. Therefore there may be as many as eight transitions under the absorption envelope.

No particular significance is attached to the values obtained for the Weiss constants of the compounds. Since the Weiss constant is composed of distortion

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[19] W. K. Robinson and S. A. Friedberg, *Phys. Rev.*, **117**, 402 (1960).

effects involving the orbital momentum as well as exchange effects,[20] it is difficult to comment considering the small values obtained.

Acknowledgments.—The authors thank Dr. Harry Gray for making available the magnetometer for low-temperature magnetic susceptibility measurements. In particular, thanks are expressed to Al Schweizer for his excellent instruction in the use of the magnetometer. Gratitude is also expressed to the National Science Foundation and the National Institutes of Health from which partial funding of the research was received.

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Trigonal Prismatic–Octahedral Coordination. Complexes of Intermediate Geometry[1]

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The synthesis and characterization of the divalent metal complexes (Zn, Ni, Co, Fe, Mn) of the ligand 1,1,1-tris(pyridine-2-aldiminomethyl)ethane (py_3TPN) are described. X-Ray diffraction studies are reported for $[Zn(py_3TPN)](ClO_4)_2$, $[Fe(py_3TPN)](ClO_4)_2$, and *cis,cis*-1,3,5-tris(pyridine-2-aldimino)cyclohexanenickel(II) perchlorate, $[Ni(py_3tach)](ClO_4)_2$. The complex $[Zn(py_3TPN)](ClO_4)_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/a$ (c unique), with a = 19.993 (21) Å, b = 17.930 (20) Å, c = 15.320 (17) Å, γ = 150.64 (5)°, and $\rho_{obsd} = 1.58$, $\rho_{calcd} = 1.59$ g cm^{-3} for $Z = 4$; $R_1 = 7.8\%$ for 1614 reflections. It was determined, from precession photographs, that the Mn, Co, and Ni complexes are isomorphous with the Zn complex. The complex $[Fe(py_3TPN)](ClO_4)_2$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$, with a = 11.827 (8), b = 21.266 (15), c = 10.667 (8) Å, and $\rho_{obsd} = 1.59$, $\rho_{calcd} = 1.58$ g cm^{-3} for $Z = 4$; $R_1 = 6.7\%$ for 1206 reflections. The complex $[Ni(py_3tach)](ClO_4)_2$ crystallizes in the noncentrosymmetric monoclinic space group Pc, with a = 15.470 (7) Å, b = 9.971 (5) Å, c = 20.503 (10) Å, β = 120.88 (2)°, and $\rho_{obsd} = 1.62$, $\rho_{calcd} = 1.60$ g cm^{-3} for $Z = 4$; $R_1 = 7.5\%$ for 1800 reflections. These complexes contain ligands that possess a trigonal axis, but are considerably distorted from octahedral geometry; angles of "twist" from such geometry are approximately 32° for $Zn(py_3TPN)^{2+}$, 28° for $Ni(py_3tach)^{2+}$, and 17° for $Fe(py_3TPN)^{2+}$. The structures of these and similar compounds are discussed in relation to their physical and spectroscopic properties and to the nature of the sexidentate ligand.

The first class of molecular complexes that was found to possess trigonal prismatic geometry were the metal tris(dithiolenes).[2] More recently, the tris(diselenetenes) have been found to exist in a similar geometry.[3] The earlier discovered metal sulfide compounds, with an infinite polymeric structure, also exist in a trigonal prismatic geometry.[4] These systems are possibly stabilized in the trigonal prismatic array by some type of S···S (Se) interaction.

For tris bidentate ligand complexes, such as the dithiolenes, the distortions from octahedral or trigonal prismatic coordination have been described[5] using two parameters (see Figure 1): (1) an angle, ϕ, describing the twist of the faces perpendicular to the threefold axis in these complexes and (2) the ratio of the distances, s/h, of the side of a triangular face to the height between the faces. These parameters are related by the ligand bite and metal–ligand bond lengths. Note, that for an octahedron $\phi = 60°$ and for a trigonal prism $\phi = 0°$.

Trigonal prismatic complexes of a different type are the "clathro chelate" systems[6] in which the ligand geometry constrains the coordination geometry of the complex. A three-dimensional ligand system developed by Holm[7] (shown in Figure 2a) exists in a trigonal prismatic geometry for the nickel complex. It is surprising that even with such a rigid ligand, other effects can cause the ligand to rotate away from its preferred conformation and $Fe(PccBF)^+$ has an average ϕ of 21°. Another "clathro chelate" had previously been synthesized[8] from tris(dimethylglyoximato)cobalt(III), which exists in a near trigonal prismatic geometry for the Co(II) complex ($\phi = 8.6°$, Figure 2b), but in an intermediate geometry for Co(III) ($\phi = 31°$).

Three systems of an open-trifurcated sexidentate type are represented in Figure 3 (a–c): (a) *cis,cis*-1,3,5-tris(pyridine-2-aldimino)cyclohexane,[9] for which the Zn(II) complex is known to possess near trigonal prismatic coordination ($\phi = 4.6°$); (b) 1,1,1-tris(pyridine-2-aldiminomethyl)ethane, of which the Fe(II) complex has been prepared[10] and the very similar 1,1,1-

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(1) Preliminary accounts of this work have appeared: E. B. Fleischer, A. E. Gebala, and P. A. Tasker, *J. Amer. Chem. Soc.*, **92**, 6365 (1970); E. B. Fleischer, A. E. Gebala, and D. R. Swift, *Chem. Commun.*, 1280 (1971).

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