chlores.[1-12] Sixfold radii of A ions[18] were used because no set of eightfold radii was available. Previously the smallest A and B ions to be found in the pyrochlore structure were Lu^{3+} and Ti^{4+}, respectively. In these new pyrochlores two new A ions, In^{3+} and Sc^{3+}, and one new B ion, Ge^{4+}, have been introduced. Although $Sc_2Ti_2O_7$ was reported to be a pyrochlore, Brisse[11] has shown that it is actually a disordered fluorite. The new phases $Sc_2Ge_2O_7$ and $In_2Ge_2O_7$ both have smaller cell dimensions than the value 9.801 quoted by Hoekstra and Siegel[9] as a "virtual lower limit" for the pyrochlore structure. Brisse and Knop[19] found that the stability of the pyrochlore structure depends upon the ratio of the ionic radii, r_A/r_B, and that the upper limit of this ratio at normal conditions is 1.55. This study indicates that pressure extends this ratio to approximately 1.8 (r_{Gd}/r_{Ge}).

The germanates are believed to be formed by taking advantage of the difference in compressibility between the oxygen anions and the A and B cations. Pressure has been used to force a smaller ion into a structure by using compressibility differences in SiO_2 (rutile),[20] Lu_2O_3 (B rare earth oxide),[21] $MgGeO_3$ (ilmenite),[22] and $InCrO_3$ (perovskite).[13] It might also be noted that $In_2Ge_2O_7$, $InCrO_3$,[13] and $InRhO_3$[13] are the first examples of compounds containing In^{3+} in greater than sixfold coordination.

It seems logical to assume that by the application of sufficient pressure one could make pyrochlores of the type $A_2Si_2O_7$. However, reaction of Sc_2O_3 and SiO_2 at 1500° and 65 kbars resulted only in the well-known $Sc_2Si_2O_7$ thortveitite phase. Apparently, higher pressures are necessary to force Si^{4+} from fourfold to sixfold coordination.

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Metal Complexes of Pyrazole

By N. A. Daugherty and J. H. Swisher

Although the behavior of imidazole as a ligand is well documented in the literature, few references are found regarding metal complexes of pyrazole, the isomer

of imidazole. Pflaum[1] has described the preparation and properties of a cobalt(II) complex of 3,5-dimethylpyrazole. Crow[2] has investigated the pyrazole complexes of cadmium(II) by polarographic techniques. The crystal structure of the complex formed between nickel chloride and pyrazole has recently been reported.[3]

The coordination chemistry of pyrazole should be of interest for comparison with the coordination chemistry of imidazole. Since pyrazole is a relatively weak base and is isoelectronic with cyclopentadiene, the possibility exists of forming π-bonded complexes analogous to ferrocene. This paper reports the preparation and properties of some transition metal complexes of pyrazole.

Experimental Section

Materials.—Pyrazole was purchased from the Aldrich Chemical Co. and was recrystallized from cyclohexane prior to use. The recrystallized material melted at 69.5–70.0°. The metal chlorides and nitrates used were Baker Analyzed chemicals. Metal tetrafluoroborates, prepared by the reaction of tetrafluoroboric acid with the appropriate metal carbonate, were recrystallized from water prior to use. Nickel perchlorate was obtained from the G. F. Smith Chemical Co. Anhydrous methanol was prepared by refluxing methanol over magnesium turnings followed by distillation. The acetonitrile used for solution spectra was Baker Analyzed material which contained 0.12% water.

Preparation of Metal Complexes.—The usual method consisted of mixing 2 ml of a 1 M solution of the metal salt with 3 or 4 ml of a 4 M pyrazole solution. Intense color changes accompanied mixing. The reaction mixtures were allowed to stand in stoppered flasks until crystallization of the complex occurred. The time required for the complex to crystallize from the solution depended on the metal salt and solvent used. Ethanol or methanol was used when crystallization from water occurred slowly. The complexes were recrystallized from the preparation solvent, collected by filtration, and washed with a small amount of ice-cold ether.

Analyses.—Copper was determined spectrophotometrically in a 2 M ammonia–ammonium chloride buffer. It was necessary to decompose the copper complexes by boiling with concentrated nitric acid prior to analysis. Nickel was determined either by the dimethylglyoxime method or volumetrically by the cyanide method.[4] Cobalt was determined by the cyanide method. Iron was determined by reduction to iron(II) with zinc amalgam followed by reaction with excess cerium(IV). The excess cerium(IV) was back-titrated with ferrous sulfate to the ferroin end point. Chloride was determined gravimetrically. Carbon, hydrogen, and nitrogen microanalyses were performed by Galbraith Laboratory, Knoxville, Tenn.

Spectra.—Solution spectra in the 380–1200-mμ region were recorded using a Cary Model 14 spectrophotometer. Reflectance spectra were obtained using a Perkin-Elmer–Hitachi spectrophotometer, Model 139, equipped with a diffuse reflectance attachment.

X-Ray Powder Patterns.—Powder patterns were obtained using a General Electric Model-BR Type 1 instrument employing nickel-filtered copper Kα radiation.

Results

The data in Table I clearly indicate that pyrazole (Pz) forms well-defined complexes with a number of transition metal ions. The complexes contained four

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<div align="center">TABLE I</div>
<div align="center">ANALYTICAL DATA OF SOME TRANSITION METAL COMPLEXES OF PYRAZOLE</div>

Complex[a]	Prepn solvent	Color	% M Calcd	% M Found	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Cl Calcd	% Cl Found
CuPz₄(BF₄)₂	H₂O	Dk blue	12.47	12.70	28.29	28.03	3.17	3.18	22.00	21.75		
CuPz₄Cl₂	H₂O	Dk blue	15.62	15.60	35.43	35.25	3.97	3.99	27.55	27.78	17.40	17.30
NiPz₆(NO₃)₂	H₂O	Lavender	9.93	10.24	36.56	36.12	4.10	4.04	33.17	33.41		
NiPz₆(BF₄)₂	H₂O	Lavender	11.63	11.62	33.74	33.81	3.78	3.83	26.24	26.53		
NiPz₆(ClO₄)₂	H₂O	Lavender	8.81	8.73	32.45	31.69	3.64	3.63	25.24	25.94		
NiPz₄Cl₂	C₂H₅OH	Lt blue	14.61	14.72	35.86	35.93	4.02	4.07	27.89	28.17	17.64	17.65
CoPz₆(NO₃)₂	H₂O	Orange-yellow	9.96	9.69	36.55	36.36	4.10	4.00	33.16	33.29		
CoPz₆(BF₄)₂	H₂O	Lt orange	9.19	9.42	33.72	33.76	3.78	3.62	26.23	26.03		
CoPz₄Cl₂	H₂O	Pink	14.65	14.38	35.84	35.97	4.02	4.05	27.87	27.95	17.63	17.41
FePz₄Cl₃	C₂H₅OH	Orange	12.85	15.23	33.17	29.70	3.72	3.29	25.79	23.28	24.48	24.44
FePz₄Cl₂	CH₃OH	Gold	14.00	13.70	36.11	36.09	4.05	3.97	28.08	28.23	17.77	18.45

[a] $Pz = C_3N_2H_4 = \begin{matrix} HC=CH \\ | \quad >NH. \\ HC=N \end{matrix}$
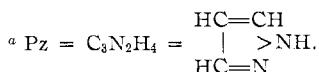
or six pyrazoles per metal ion, depending upon the metal ion and the anion present.

The maximum number of pyrazoles that coordinate to copper(II) appears to be 4, even when the anion is a very poor ligand.

Nickel(II) forms complexes containing either four or six pyrazoles per metal ion, depending upon the anion of the nickel salt used. A coordination number of 6 results when the nickel salt is a nitrate, perchlorate, or tetrafluoroborate. When nickel chloride is used, only four pyrazoles coordinate per nickel ion.

Table II shows the position of the maxima in the absorption spectra of the nickel(II) complexes, both in solution and in the solid state. In acetonitrile solution the spectra of $NiPz_6(ClO_4)_2$ and $NiPz_6(BF_4)_2$ are similar and compare well to the reflectance spectrum of solid $NiPz_6(BF_4)_2$. The spectrum of $NiPz_4Cl_2$ in acetonitrile differs from the spectra of the other nickel complexes. Addition of pyrazole to an acetonitrile solution of $NiPz_4Cl_2$ causes a shift in the position of the absorption maxima, resulting in a spectrum which closely resembles that of $NiPz_6(BF_4)_2$. The addition of pyrazole to acetonitrile solutions of $NiPz_6(BF_4)_2$ results in the precipitation of some of the complex but does not appreciably alter the spectrum of the solution that remains above the solid. The acetonitrile solutions of all of the complexes show some deviation from adherence to Beer's law. In aqueous or methanolic solutions all of the complexes have similar spectra.

Cobalt(II) also forms complexes containing four or six pyrazoles per cobalt ion, depending upon the anion present. X-Ray powder patterns indicate that the complexes derived from cobalt chloride and nickel chloride are isomorphous as are the complexes derived from the corresponding tetrafluoroborates. However, the complexes derived from cobalt nitrate and nickel nitrate are not isomorphous. When solutions of cobalt(II) chloride and pyrazole are treated with hydrogen peroxide, dark orange-red solutions result indicating the feasibility of making the cobalt(III) complex. Isolation of the cobalt(III) complex has not yet been accomplished.

The iron(II) and iron(III) complexes prepared from the chloride salts apparently contain four pyrazoles

<div align="center">TABLE II</div>
<div align="center">ELECTRONIC ABSORPTION SPECTRA OF SOME</div>
<div align="center">NICKEL(II) COMPLEXES OF PYRAZOLE</div>

Complex	State	ν_{max}, cm⁻¹		
NiPz₄Cl₂	CH₃CN soln[a]	8,300	15,900	25,600
NiPz₆(BF₄)₂	CH₃CN soln[a]	11,000	17,800	28,200
NiPz₆(BF₄)₂	CH₃CN soln[b]	11,000	17,900	29,400
NiPz₆(ClO₄)₂	CH₃CN soln[a]	10,900	17,700	28,200
NiPz₄Cl₂	Solid	13,200	16,400	
NiPz₆(BF₄)₂	Solid	10,800[c]	17,900	28,000

[a] Complex concentration *ca.* 0.01 *M*. [b] Concentration of complex *ca.* 0.005 *M* in 1.0 *M* Pz solution [c] We are indebted to Cary Instruments for the spectrum showing the position of this band.

per metal ion. The analytical results for the iron(III) complex are poor, apparently due to an impurity which cannot be removed by recrystallization.

During the course of this work it was observed that interactions also occur between pyrazole and manganese(II), vanadium(IV), and chromium(III) in aqueous solution.

Discussion

In spite of the fact that pyrazole is a relatively weak base ($pK_a = 2.47$ *vs.* 6.95 for imidazole[5]), it readily coordinates with many metal ions in the first transition series. When anions of moderate complexing ability are present, only four pyrazoles coordinate per metal ion. In the absence of anions which may compete effectively as ligands, coordination numbers of 6 are possible.

The spectral evidence is in accord with an octahedral geometry for the $NiPz_6{}^{2+}$ ion. The ratio ν_2/ν_1 for the complex is 1.66, which is nearly the same value observed for tris(ethylenediamine)nickel(II) ion, and compares well with the calculated value of 1.8,[6] which is one of the distinguishing features of octahedral complexes.

The position of the low-energy band in the reflectance spectrum of $NiPz_6(BF_4)_2$ leads to a value[7] of 10,800 cm⁻¹ for $10Dq$ for pyrazole ligands. Thus, pyrazole

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(7) R. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 168, 169.

occupies about the same position as ammonia in the spectrochemical series.

The effect of added pyrazole on the solution spectra of NiPz₄Cl₂ and NiPz₆(BF₄)₂ and the observed deviations from Beer's law indicate that some dissociation of the complex occurs even in acetonitrile solutions.

This study does not allow much to be said concerning the manner in which pyrazole is bound to the metal ion. The observed coordination numbers make π bonding appear to be unlikely. A more likely possibility is that bonding is through the "pyridine nitrogen," as is suggested for imidazole complexes.[8]

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Replacement of Carbon Monoxide on Monosubstituted Molybdenum Carbonyl Derivatives

BY FRANCO ZINGALES, FELICE FARAONE, PAOLO UGUAGLIATI, AND UMBERTO BELLUCO

Even though a great amount of work has been done in the past year on substitution reactions of derivatives of the group VI and VII metal carbonyls, scant information is available concerning a systematic investigation of the *cis* effect in such reactions. On the ground of mainly preparative and infrared spectral observations, this effect was hitherto believed to be of rather minor importance inasmuch as two groups in *cis* positions are unable to compete for d electrons of the metal on as favorable terms as they do when in *trans* positions. As for the kinetic behavior of these systems, no appreciable *cis* effect appeared to be operative in the reactions of *cis*-CO dissociation from *cis*-Mn(CO)₄-BrAs(C₆H₅)₃ and from Mn(CO)₅Br.[1] An unusual detectable *cis* effect was displayed by the reactions of M(CO)₄BrL with L′ to give *cis*-M(CO)₃BrLL′ (M = Mn, Re). For instance, the rate constants for the dissociative path of the manganese complex at 40° range from 3.1 × 10⁻⁵ sec⁻¹ for L = P(OC₄H₉)₃ to 77 × 10⁻⁵ sec⁻¹ for L = P(C₆H₅)₃.[1] For the analogous reactions of rhenium compounds, the dissociative rate constants vary from 2.9 × 10⁻⁵ sec⁻¹ for P(n-C₄H₉)₃ to 14 × 10⁻⁵ sec⁻¹ for P(C₆H₅)₃ up to 87 × 10⁻⁵ sec⁻¹ for γ-picoline.[2] Where the donor atom of the coordinated ligand L is the same (*e.g.*, phosphorus), mainly steric properties

(1) R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).
(2) F. Zingales, U. Sartorelli, and A. Trovati, *ibid.*, **6**, 1246 (1967).

of L have been invoked to account for this unprecedented *cis* effect. In order to throw some light on the factors by which a *cis* effect, if any, is governed, we have investigated the replacement of CO in monosubstituted molybdenum carbonyl derivatives of the type Mo(CO)₅L, by different neutral entering groups L′ leading to *cis*-Mo(CO)₄LL′. The ligands L have been so chosen as to have about the same steric requirements, yet different σ-donor abilities.

Experimental Section

Preparation and Purification of Materials.—Pyridine, 4-picoline, 3-chloropyridine, and 3,4-lutidine (British Drug Houses) were distilled before use. Triphenylphosphine, triphenylarsine, and triphenylstibine, commercial reagent grade, were recrystallized from petroleum ether (bp 40–70°). Toluene (Analar, British Drug Houses) was refluxed over sodium wire and fractionally distilled before use in the kinetic studies.

The compounds Mo(CO)₅L and *cis*-Mo(CO)₄L₂ (L = P(C₆H₅)₃, As(C₆H₅)₃, Sb(C₆H₅)₃) were prepared following the methods given in the literature.[3,4] The compounds Mo(CO)₅L (L = pyridine, 4-picoline) were prepared by refluxing Mo(CO)₆ and a slight molar excess of the pyridine in a mixture of n-heptane and n-pentane boiling at 65°, under a nitrogen atmosphere for 6 hr. Under vacuum the solution was evaporated to dryness. The residue was washed with portions of pentane and the washings were cooled to −80°. The green-yellow crystals were filtered and dried. Excess Mo(CO)₆ was sublimed off at 50° under vacuum. The compounds *cis*-Mo(CO)₄L₂ (L = pyridine, 4-picoline) were prepared according to Kraihanzel and Cotton.[5]

The identity and purity of all of these compounds were confirmed by their carbon, hydrogen, and nitrogen analyses and by their infrared spectra.

Kinetic Studies.—All of the reactions were carried out by using an excess of the entering group in order to assure pseudo-first-order conditions. The reactions were followed by monitoring the disappearance of the highest frequency carbonyl stretching band of the starting material (*ca.* 3 × 10⁻³–2 × 10⁻² M). Measurements were taken over about 2 half-lives, since in all of the reactions an equilibrium was reached. However, the A_∞ value was taken as that of the base line, corresponding to the theoretically complete disappearance of the band. To make sure that in any case the *cis* isomer M(CO)₄LL′ only was the reaction product, some runs were carried out in other solvents where better band resolution allowed such characterization. Kinetic data for such solvents (n-heptane, carbon tetrachloride, etc.) are not reported here, though, owing to the very low solubility of the examined carbonyl derivatives. Unfortunately, attempts to prepare and isolate the "mixed" reaction products *cis*-Mo(CO)₄LL′ as pure substances failed since the reactions led to equilibrium mixtures. The infrared data were obtained with a Perkin-Elmer Model 621 spectrophotometer. The reactions were carried out under nitrogen in an aluminum-foil-wrapped vessel fitted with a serum cap. More details about this method have been given previously.[6] Reaction mixtures for which the product was not isolated gave infrared spectra analogous to the disubstituted derivatives *cis*-Mo(CO)₄L₂ (Table I).

Results and Discussion

In Table I there are listed the CO stretching frequencies of the molybdenum carbonyls investigated along with those of authentic samples of products independently prepared when possible. By allowing Mo-(CO)₅L to react with neutral ligands L′, *cis*-Mo(CO)₄-LL′ complexes only have been obtained. These could

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(4) M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).
(5) C. S. Kraihanzel and F. A. Cotton, *ibid.*, **2**, 533 (1963).
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