are well within 95% confidence limits of the new values. If a significant disagreement had been observed at this point, the whole procedure could be repeated to give self-consistency.

Conclusions

The results of this study indicate that the nmr line broadening caused by the $(H_2O)_5CrN_3^{2+}$ ion is largely associated with water proton exchange. The failure to detect exchange from coordinated N_3H may be due to the high acidity of the coordinated acid or to a long relaxation time for the proton of coordinated N_3H. Therefore it is not possible to establish even any limits for the acidity of coordinated hydrazoic acid.

The rate constants and ΔH^* values in Table I show the expected variation, if only charge effects are considered, when compared to rates for $Cr(OH_2)_6^{3+}$ obtained by Swift, *et al.*,[4,5] and in these laboratories[9] using nmr line broadening, and by Rich, Cole, and Eyring[10] using the dissociation field relaxation method. It should be noted that a recent T_1 nmr study of Melton and Pollak[11] has yielded quite different exchange rate parameters.

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Molybdenum(II)–Isocyanide Complexes

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MoL_5X_2 (L = isocyanide, X = Cl, Br) are prepared from $Mo(CO)_4X_2$ and the ligand. They are characterized through infrared and nuclear magnetic resonance spectra and conductance data. The presence of a possible seven-coordinate molybdenum(II) is suggested.

While zerovalent molybdenum–isocyanide complexes, *e.g.*, $Mo(CO)_{6-n}L_n$ ($n = 1, 2, 3, 6$)[1–5] and $Mo(NO)_2L_2Cl_2$[6] (L = isocyanide), are well known, molybdenum(IV) compounds are dubious, and only three complexes are known[7] where molybdenum has the formal oxidation state +2: these complexes contain a π-C_5H_5 ring. The recent preparation of $Mo(CO)_4X_2$ compounds[8] prompted us to try their reaction with isocyanide and a novel type of molybdenum(II) compounds, MoL_5X_2, is reported here.

Experimental Section

Isocyanides were prepared according to Ugi.[9] Molybdenum tetracarbonyl halides were prepared according to Colton[8] and used immediately.

Molybdenum analysis[10] was carried out gravimetrically as $MoO_2(oxinate)_2$, after destroying the sample with H_2SO_4–KNO_3; halogen analysis, as silver halide, after decomposing the sample in a melt of KNO_3–Na_2CO_3.

Diamagnetism in the solid state was checked with a Gouy balance. The ^1H nmr spectra were recorded by Dr. G. Bonora on a Perkin-Elmer R-10 instrument at 60.0 Mc; the solvent was always $CDCl_3$, with tetramethylsilane as internal standard. Molecular weight determinations were carried out on a Mechrolab osmometer in chloroform solution at 37°.

The compounds are stable in the solid state but not in solution as evidenced, *inter alia*, by the change of molar conductance with time.

Pentakis(cyclohexyl isocyanide)dibromomolybdenum(II).—Cyclohexyl isocyanide (2.5 ml) was dissolved in acetone (3 ml); the solution was added to a solution of tetracarbonyldibromomolybdenum(II), prepared[8] from hexacarbonylmolybdenum(0) (1.0 g), in acetone (*ca.* 100 ml). After 10 min the solution was concentrated under reduced pressure; the scarce precipitate which formed was filtered and identified as $Mo(CO)_6$ by the infrared spectrum. The filtered solution was evaporated to dryness under vacuum; the residual thick oil was dissolved in ethanol and treated with ether, under scratching. A yellow powder was obtained, filtered (0.79 g), and crystallized from ethanol–diethyl ether to yield the pure yellow compound. *Anal.* Calcd for $C_{30}H_{55}Br_2MoN_5$: C, 52.45; H, 6.9; N, 8.7. Found: C, 52.63; H, 7.51; N, 8.55. ν_{max} 2136 cm^{-1}, very broad and unresolved ($CHCl_3$). A freshly prepared 6.54×10^{-4} *M* nitrobenzene solution gave a conductance value of 33 ohm^{-1} cm^2 mol^{-1}, which dropped to 16.1 after 18 hr.

Pentakis(*p*-tolyl isocyanide)dibromomolybdenum(II).—An acetone (40 ml) solution of tetracarbonyldibromomolybdenum(II), prepared[8] from hexacarbonylmolybdenum(0) (1.0 g), was added to an acetone (3 ml) solution of *p*-tolyl isocyanide (2.5 ml).

The yellow precipitate was then filtered and crystallized from dry chloroform–petroleum ether (bp 40–70°) to yield a yellow compound (0.37 g), mp 157°. *Anal.* Calcd for $C_{40}H_{35}Br_2MoN_5$: C, 57.0; H, 4.15; N, 8.32; Br, 19.0. Found: C, 56.21; H,

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4.18; N, 8.07; Br, 19.4. The conductance value of a 6.0×10^{-1} *M* nitrobenzene solution was found to be 2.1 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ immediately and 5.24 after 48 hr. The nmr spectrum showed signals at τ 2.74 and 7.59 with area ratio 1.34:1; $\nu_{\max}$(Nujol): 2157 (vw), 2118 (m), 2102 (s), 2072 (s), 1499 (m), 1459 (w, br), 1427 (vw), 1369 (vw), 1358 (vw, br), 1007 (vw), 840 (sh), 819 (s), 815 (m), 811 (s), 800 (w), 747 (w, br), 721 (m), 710 (m), 695 (vw), 642 (m), 508 (sh), 498 (s), 472 (sh), 470 (w, br), 460 (m), 451 (m), 448 (sh), 418 (w, br), 319 cm^{-1} (vw); $\nu_{\max}$($CHCl_3$): 2118 (s), 2076 (s, br), 2033 cm^{-1} (m).

Pentakis(*p*-tolyl isocyanide)dichloromolybdenum(II).—A fresh benzene solution (350 ml) of tetracarbonyldichloromolybdenum(II) was prepared[8] starting from hexacarbonylmolybdenum(0) (10 g) and was immediately treated with a benzene solution (30 ml) of *p*-tolyl isocyanide (22.2 g). Gas was evolved; then the flask was repeatedly evacuated during 2 hr. The solution was then concentrated down to *ca.* 100 ml under vacuum at room temperature; petroleum ether was added and the yellow precipitate (1.4 g) was isolated by filtration. The yellow compound was purified by crystallization from chloroform–petroleum ether; mp 164° after some decomposition at 155°. *Anal.* Calcd for $C_{40}H_{35}Cl_2MoN_5$: C, 63.8; H, 4.66; N, 9.31; Mo, 12.75; Cl, 9.44; mol wt, 752. Found: C, 62.77; H, 4.59; N, 9.10; Mo, 12.69; Cl, 9.30; mol wt ($CHCl_3$, 8.37% w/w), 828. It is soluble in acetonitrile, nitrobenzene, chloroform, and benzene, less soluble in acetone, and insoluble in methanol and ethyl acetate. The conductance values were found to be 3.11, 76.8, and 80.8 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ for a 6.5×10^{-4} *M* nitrobenzene solution and for a 6.1×10^{-4} and a 1.62×10^{-4} *M* acetonitrile solution, respectively. The two former values were found to be 5.75 and 61.5 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ after 18 hr. The compound is diamagnetic in the solid state; its nmr spectrum showed signals at τ 2.79 and 7.65, with an area ratio of 1.4:1; $\nu_{\max}$(Nujol): 2158 (w), 2121 (s), 2102 (s, br), 2074 (s), 2036 (m), 1918 (w, br), 1507 (vw), 1498 (s), 1450 (m, br), 1404 (vw), 1372 (m, br), 1310 (sh), 1207 (vw), 1098 (vw, br), 1015 (sh), 1012 (m), 840 (vw), 822 (s), 815 (sh), 811 (s), 735 (sh), 722 (m), 711 (w), 696 (vw), 642 (w), 511 (m), 498 (s), 473 (m, br), 461 (m), 448 (m, br), 418 (w, br), 318 (vw), 285 cm^{-1} (w, br); $\nu_{\max}$($CHCl_3$): 2133 (s), 2079 (s, br), 2033 cm^{-1} (m).

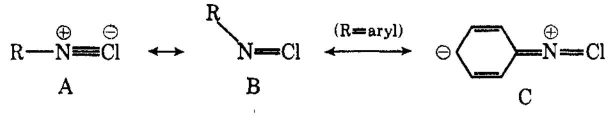
Results and Discussion

The reaction of an isocyanide with a fresh solution of $Mo(CO)_4X_2$ (X = Cl, Br) brought about carbon monoxide displacement. After working up the reaction mixture, stable yellow compounds were isolated, for which the analytical data suggested an MoL_5X_2 formula.

The reactivity of $Mo(CO)_4X_2$ toward isocyanide is quite different from that toward other ligands having poor or no π-bonding ability such as $E(C_6H_5)_3$ (E = P, As, Sb)[11] or amines,[12] which do not displace carbon monoxide completely.

The compounds obtained by carbonyl replacement in $Mo(CO)_4X_2$ by various ligands can be[12a] high spin or low spin: according to the high ability of the isocyanide group to cause d-orbital splitting, the compounds prepared here are diamagnetic, both in the solid state and in solution.

The infrared spectra of the compounds show the required[13] ν(CN) absorptions, which are broad and in one case overlap to give a single very broad band; therefore, they cannot be used to suggest a structure on the basis of the group theory. However, their average position is in the same range or is lower than ν(CN) of the free ligand. The value and the sign of $\Delta\nu$ (*i.e.*, $\nu(CN)_{\text{free ligand}} - \nu(CN)_{\text{bonded ligand}}$) suggest a moderate amount of π back-donation from the low-valent metal atom to the ligand: $\Delta\nu$ is of the order $+60 + 200$ cm^{-1} in the chromium(0) complexes,[4] where the amount of π bonding is remarkable and is $-60 - 150$ cm^{-1} in aluminium[14] or boron[15] complexes where no π but only σ bonding is possible. The infrared spectra do not show any band which could be assigned to Mo=O stretching, the presence of which would raise the oxidation number to 4. Correspondingly, the halogen-sensitive bands at 285 (X = Cl) and 209 cm^{-1} (X = Br) are observed nearly in the same position as the equally halogen-sensitive bands in other molybdenum(II) complexes, *e.g.*, $Mo(CO)_3(P(C_6H_5)_3)_2X_2$ (293 for X = Cl and 209 cm^{-1} for X = Br). The complexes containing aromatic isocyanide as ligands were not electrolytes in nitrobenzene solution, suggesting that seven-coordinate molybdenum(II) is present. On the other hand, $Mo(c\text{-}C_6H_{11}NC)_5Br_2$ is an electrolyte in the same solvent. When the aromatic group R is replaced by an aliphatic group, the contribution of the canonical form C vanishes and the C–N bond order is raised, both in the free molecule and in the complex. This fact is reflected by ν(CN) stretching frequencies: $\nu(CH_3C_6H_4NC)$ 2125, $\nu(C_6H_{11}NC)$ 2138, and ν_{av} 2080 and 2136 cm^{-1} for the corresponding molybdenum(II) complexes. The higher contribution from A, when R is an aliphatic group in comparison to the case when R is an aromatic group, affects also the electron density on the metal atom; consequently, in the case of cyclohexyl isocyanide complexes the equilibrium



$$MoL_5Cl_2 + \text{solvent} \rightleftharpoons MoL_5X(\text{solvent})^+ + X^-$$

is shifted to the right. A shift to the right can also be caused by a good solvating medium, such as acetonitrile, even when L is an aryl isocyanide.

There is a remarkable difference between the reactions of $Mo(CO)_6$ and of $Mo(CO)_4X_2$ with isocyanides. The former gives only $Mo(CO)_{6-n}L_n$ (n = 1, 2, 3),[2-5] while the latter undergoes complete carbon monoxide replacement. The replacement of a CO group in $Mo(CO)_6$ with a less π-accepting ligand, such as L, yields a compound which has a bigger electronic density on the Mo atom than $Mo(CO)_6$; a nucleophilic attack on $Mo(CO)_5L$ becomes more difficult. On the other hand, an S_N1 mechanism on $Mo(CO)_5L$ requires a five-coordinate intermediate, either $Mo(CO)_5$ or $Mo(CO)_4L$. The former is favored[16] but cannot give rise to disubstitution; the latter requires that a Mo–CO bond is

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labilized, while isocyanide is considered a nonlabilizing ligand.[16,17]

As for molybdenum(II) compounds the formal positive charge, the ability to reach coordination number 7, and the possibility of a more complicated mechanism[18] than an SN1 or an SN2 remove the obstacles to ready and complete substitution of CO groups by isocyanides.

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Manganese Porphyrin Complexes. IV. Reduction of Manganese Porphyrins[1]

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The polarographic reduction of a number of (anion)porphyrinmanganese(III) complexes was carried out at the dropping mercury electrode in acetonitrile and dimethylformamide solution. The polarograms show three separate reversible one-electron reductions which can be ascribed to the Mn(III) → Mn(II) reduction at −0.15 to −0.49 V (*vs.* sce) and to the first and second porphyrin reductions at −1.14 to −1.67 and −1.62 to −2.05 V, respectively. The half-wave potentials are dependent on the anion and the porphyrin. The porphyrin order, $-E_{1/2}$, for the three waves is etioporphyrin I $\geq$ mesoporphyrin IX dimethyl ester $>$ deuteroporphyrin IX dimethyl ester $\geq$ hematoporphyrin IX dimethyl ester $>$ protoporphyrin IX dimethyl ester $>$ $\alpha,\beta,\gamma,\delta$-tetraphenylporphine $>$ methyl pheophorbide$_a$. The dependence of the Mn(III) → Mn(II) half-wave potentials on the anion was determined for the etioporphyrin I and protoporphyrin IX dimethyl ester derivatives. The anion order, $-E_{1/2}$, is $F^- > OCN^- \geq N_3^- \geq OAc^- > OH^- \geq Cl^- > SCN^- \geq Br^- > I^-$. The electronic spectra of chemically generated manganese(II) complexes were also measured.

The role that manganese plays in the photosynthetic liberation of oxygen from water is undoubtedly linked to the ability of the metal ion to function as a redox catalyst.[2] The utility of the metal ion in this process depends on the potential resulting from the changes between the oxidation states and the availability of suitable oxidation states. Both of these are a function of the ligand field around the metal ion.[3] Although the binding site of manganese in the photosynthetic unit has not been assigned, the donor atoms surrounding the metal will most probably be nitrogen or oxygen (or less likely sulfur) of a prosthetic group or of an apoprotein.[4] The ligand field may be composed of all of one kind of donor atom or a mixture of several kinds. Good model ligands for the nitrogen donor prosthetic group are porphyrins. In addition to being peripatetic biological ligands, they form complexes with manganese(II), manganese(III), and manganese(IV).[5] The Mn(III) → Mn(II) potential has been determined for a few cases either by titration with dithionite or by polarographic reduction. The hydroxide complexes studied have included those of mesoporphyrin IX,[6] hematoporphyrin IX,[5,7] hematoporphyrin IX dimethyl ester,[5,7] and methyl pheophorbide$_a$.[8] No detailed assessment of the factors that influence the magnitude of the redox potential was made in these studies.

We have studied the polarography of a number of manganese(III) porphyrins with a variety of anions and porphyrins. (See Figure 1.) For the case of reversible reductions, polarography provides a convenient way of determining redox potentials.[9] By examining complexes with porphyrins of varying basicity and with axial anions of differing coordinating characteristics, we can determine the relative importance of in-plane and axial interaction on the redox potentials of manganese(III) porphyrins.

Experimental Section

Materials.—Manganese porphyrin complexes were prepared and purified according to the procedure set out in previous papers.[10,11] Tetra-*n*-propylammonium perchlorate was prepared by a standard method.[12] Acetonitrile was purified according to the procedure of Coetzee.[13] Dimethylformamide was refluxed

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