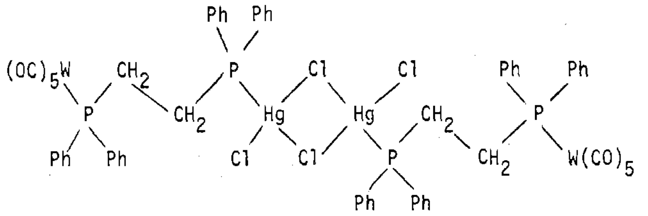

are shown in Figure 1.

The $^{1}J_{^{195}Pt-^{31}P}$ value of 3642.3 Hz establishes the structure of $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$ to be cis rather than trans. The magnitude of the coupling compares well with that previously recorded for *cis*-$[(C_6H_5)_2(C_2H_5)P]_2PtCl_2$ (3640 Hz).[13] Square planar platinum(II) complexes of the trans configuration characteristically have coupling constants which are much smaller in magnitude than those of the cis configuration. For example, the value for *trans*-$[(C_2H_5)_2(C_6H_5)_2P]_2PtCl_2$ is 2482 Hz.[13]

For the purpose of determining the magnitude of $^{2}J_{PP}$ the platinum complex may be treated as an AA'XX' system. Spin systems of the type $AA'X_nX'_n$ have been discussed in detail by Harris.[7] For the platinum complex one can observe both the A and X parts in the ^{31}P spectrum. It is reasonable to assume that $J_{XX'}$ is zero since these nuclei are so far removed from each other. Both the X and A parts of the XX'AA' spectrum have three pairs of lines centered about $\nu_{(X)}$ and $\nu_{(A)}$, respectively (see Figure 1). Half of the total intensity lies in doublets with separations $N = |J_{AX} + J_{AX'}|$ and $N = |J_{AX} + J_{A'X}|$. The remaining intensity is divided between one pair of inner lines and one pair of outer lines for each part of the two-part spectrum. The quantity N was measured to be 43.6 Hz. From the separation of inner lines and outer lines $^{2}J_{PP}$ was determined to be 14.3 Hz. The absolute value of $^{5}J_{PP}$ was calculated to be smaller than experimental error.

The ^{31}P spectrum of the mercury complex is first order (see Figure 1). The magnitude of $^{1}J_{^{199}Hg-^{31}P}$ establishes the dimeric nature of the mercury complex. The dimers, $[(C_4H_9)_3P]_2Hg_2Cl_4$ and $[(C_4H_9)_2(C_6H_5)P]_2Hg_2Cl_4$, are reported to have mercury–phosphorus coupling constants of 7446 and 7514 Hz, respectively, while the monomers $[(C_4H_9)_3P]_2HgCl_2$ and $[(C_4H_9)_2(C_6H_5)P]_2HgCl_2$ have couplings of 5078 and 5035 Hz, respectively.[14]

In complexes of the type $R_3PW(CO)_5$ it is well established that the tungsten–phosphorus coupling constants increase as the electronegativities of the substituents on phosphorus increase.[15,16] It is apparent from the values of the tungsten–phosphorus coupling constants that the electronegativities of the substituents $CH_2CH_2P(C_6H_5)_2$, $CH_2CH_2P(O)(C_6H_5)_2$, $CH_2CH_2P(C_6H_5)_2Hg$, $CH_2CH_2P(C_6H_5)_2Pt$, and $CH_2CH_2P^+(C_6H_5)_2C_4H_9$ are all very similar.

The formation of the oxide, $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, as a minor product during the platinum complex synthesis was unexpected (see Experimental Section) and apparently is catalyzed by the presence of Pt(II). The P═O stretching occurs as a doublet (1168 and 1195 cm^{-1} in Nujol) and appears to be very much like the oxide spectra reported by Ercolani.[17] For the oxide one observes two separate ^{31}P resonances appearing as doublets, both downfield from 85% phosphoric acid, and one is flanked by tungsten–phosphorus satellites. The resonance at −13.3 ppm, assigned to the phosphorus attached to tungsten, agrees well with −11.4 ppm found for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)$ and −15.2 ppm for $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6]^-$. The chemical shift at −31.6 ppm is assigned to phosphorus coordinated to oxygen, consistent with that reported for $(C_6H_5)_2(O)P(CH_2)_5P(O)(C_6H_5)_2$ (−31.8 ppm).[18]

In conclusion the ligand $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ has been shown to react with K_2PtCl_4 and $HgCl_2$ to yield stable, soluble complexes of high molecular weight. The ligand also provides a unique method of determining phosphorus–phosphorus coupling constants of chemically equivalent phosphorus nuclei.

Registry No. $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, 35324-76-6; $(OC)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2C_4H_9[PF_6^-]$, 39248-09-4; $(OC)_5WP(C_6H_5)_2CH_2CH_2P(O)(C_6H_5)_2$, 52843-30-8; $[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2Hg_2Cl_4$, 52843-29-5; *cis*-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]_2PtCl_2$, 52873-47-9; ^{31}P, 7723-14-0.

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Rapid Oxygen Exchange between $[Mo(O)(OH)(CN)_4]^{4-}$ and Water

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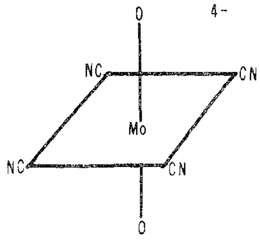
For many years there has been confusion regarding the composition and structure of the species present in solution when $K_4[Mo(O)_2(CN)_4]$ is dissolved in water.[1-4] In particular, questions regarding the acid–base behavior of the ion and the coordination number (basic structures I or II) have not been completely settled. Recently the solid structures of two of these ions have been determined[5] ($[Mo(O)(OH)(CN)_4]^{3-}$ and $[Mo(O)(OH_2)(CN)_4]^{2-}$) by X-ray techniques. We had intended to use ^{18}O measurements to obtain information about the coordination number of these substances in solution and to study the kinetics of isotopic oxygen exchange as a function of solution composition. However, as will be shown, the isotopic water exchange under obtainable conditions is too rapid to allow structural or kinetic information to be obtained.

Results and Discussion

The treatment of $K_3[Mo(O)_2(CN)_4]$ with ^{18}O-enriched water at 85–90° for 10 min and the subsequent isolation of the ion as anhydrous $K_3[Mo(O)(OH)(CN)_4]$ resulted in the complex ion having an ^{18}O content equal to that of the final



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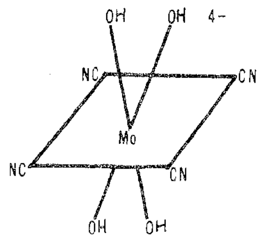

II

solvent. For example in one experiment the final values of R_N were 0.02354 (complex) and 0.02361 (solvent). This establishes that exchange is complete under the above-stated conditions.

At 0° four types of experiments were carried out to find conditions where the rate of exchange could be followed. Other than temperature, the variables were basicity, concentration, and mode of sampling. The solution basicity controls the relative amounts of the exchanging species: *i.e.*, $[Mo(O)_2(CN)_4]^{4-}$, $[Mo(O)(OH)(CN)_4]^{3-}$, $[Mo(O)(OH_2)(CN)_4]^{2-}$ with decreasing basicity ($K_{a_1} = 1.2 \times 10^{-11}$ $K_{a_2} = 6.3 \times 10^{-13}$).[5] Solutions containing predominantly the first species are not obtainable except in ~1.5 M OH^-, and solutions of the last species tend to lose CN^- at a measurable rate. Thus these experiments were limited to having mostly $[Mo(O)(OH)(CN)_4]^{3-}$ present during the exchange studies. Since oxygen exchange may be catalyzed by precipitating ions or by a change in solvent composition, several techniques were used to determine the extent of exchange. Two sets of experiments were carried out for each method and several complex samples were used with consistent results.

A. The results of experiments in which a $K_3[Mo(O)(OH)(CN)_4]$ solution was treated with enriched water and the complex precipitated with ethanol are given in Table IA. For no initial exchange the value of R_N would be 4.02×10^{-3} and would increase with time. In fact, complete exchange was observed in 90 sec.

B. A representative run in which a solution of $K_4[Mo(O)_2(CN)_4]$ is treated with $H_2{}^{18}O$ and the solvent sampled is given in Table IB. Again exchange is complete in the shortest time used.

C. Utilizing the ^{18}O-enriched oxohydroxo complex and dissolving it in normal water containing CN^- gave the results in Table IC when the complex was isolated with the $[Cr(en)_3]^{3+}$ precipitant. Zero exchange at 72 sec would have given an R_N of 23.54×10^{-3}.

D. When the $[Cr(en)_3]^{3+}$ salt was sampled as a function of time from a solution of enriched $K_3[Mo(O)(OH)(CN)_4]$ and normal water, the data in Table ID resulted. These show exchange to be complete in 35 sec.

The conclusion of these experiments is that oxygen exchange with water on $H_nMo(O)_2(CN)_4{}^{(4-n)-}$ is rapid ($t_{1/2} < 1$ min) in moderately concentrated solutions (0.1–2 M) in the presence of 0.001–1.5 M OH^-. Since in one of the experiments no physical or chemical change occurred during sample separation (except for a small concentration change), the exchange was probably not caused by the method of sampling. The presence of free CN^- had no effect.

Thus it is not possible to distinguish by this technique whether the ion in aqueous solution takes form I or II. The data do show that some means for making the complex oxygens and those of the solvent equivalent either in an activated complex or in a stable complex ion is easily available and both structures are consistent with these observations.

Also of interest is the apparent inverse relationship which appears to exist between the rate of oxygen exchange and the oxidation state of the metal: Mo(IV) > Re(V) ~ Np(V) > Os(VI) ~ Np(VI) ~ Pu(VI).

Table I. Oxygen-Exchange Data for H_2O–$[Mo(O)(OH)(CN)_4]^{3-}$

Time, sec	10^3R_N	Time, sec	10^3R_N
A. 0°, $R_N(K_3[Mo(O)(OH)(CN)_4]$ initial solution) = 4.02×10^{-3}, $R_N(H_2O$ added) = 34.8×10^{-3}, R_N(final solvent) = 33.7×10^{-3}, [Complex] = 1.10 M, pH 11.5			
90	33.7[a]	1380	33.3
138	33.4	1 hr (room temp)	33.6
240	33.1		
B. 0°, $R_N(K_4[Mo(O)_2(CN)_4]$ = 4.01×10^{-3}, $R_N(H_2O$ added) = 28.12×10^{-3}, Moles of Complex = 1.964×10^{-3}, Moles of H_2O = 5.56×10^{-2}			
118	26.42[b]	3264	26.44
239	26.46	53.400	26.34
497	26.41	∞(heat)	26.48
1390	26.44	$K_3[Mo(O)(OH)(CN)_4](s)$	26.14
C. 0°, $R_N(K_3[Mo(O)(OH)(CN)_4])$ = 23.54×10^{-3}, R_N(solvent) = 4.00×10^{-3}, 25.0 g of H_2O, 0.05 g of NaCN, 0.11 M Complex, pH 11.0			
72	4.03[c]	1400	4.02
512	4.06	2500	4.06
930	4.02	10 min at 90°	4.03
D. 0°, $R_N(K_3[Mo(O)(OH)(CN)_4])$ = 22.9×10^{-3}, R_N(solvent) = 4.01×10^{-3}, 20.0 g of H_2O, 0.18 M Complex, pH >11			
35	4.07[c]	260	4.10
65	4.13	520	4.16
122	4.14	10 min or ∞ at 90°	4.12
180	4.09		

[a] All R_N of $K_3[Mo(O)(OH)(CN)_4]$. [b] All R_N (except the last) of solvent water. Calculated number of oxygens per complex ion exchanged from stoichiometric relationships 2.17, 2.09. [c] All R_N of $[Cr(en)_3][Mo(O)(OH)(CN)_4]$.

Experimental Section

Compounds. $K_4[Mo(O)_2(CN)_4]\cdot 2H_2O$ was prepared and purified by the method of Jakob and Turkiewicz[6] as modified by Robinson.[5] Dehydration at <0.1 mm and 100° gave a tan anhydrous product with an acid–base equivalent weight of 195 ± 4 (calcd 194.2).

$K_3[Mo(O)(OH)(CN)_4]$ was prepared by dissolving the dioxo salt in the minimum amount of water and precipitating the blue product with methanol. It was washed with ethanol and ether and the precipitation repeated. After drying at <0.1 mm and 110° it gave an acid–base equivalent weight of 355 ± 7 (calcd 350.3). Oxidation of the product to Mo(VI) with $[Fe(CN)_6]^{3-}$ gave a formula weight of 352 ± 3 (calcd 350.3).

Purity problems were encountered initially due to $MoO_4{}^{2-}$ and/or $CO_3{}^{2-}$ formed by reaction with air. Their presence was easily discerned by the ir spectra. The problem was alleviated when a purified nitrogen atmosphere was used throughout the preparation and purification.

$K_3[Mo(^{18}O)(^{18}OH)(CN)_4]$ was prepared by warming 5.0 g of $K_4[Mo(O)_2(CN)_4]$ with 0.05 g of KCN and 5.0 ml of H_2O at 85–90° for 10 min. The addition of absolute ethanol gave a blue oil which upon repeated extraction gave a finely divided blue solid. It was washed with ether, air-dried, and the dried under vacuum for 2 hr. Analysis of the compounds is given in ref 5.

Exchange Experiments. Efforts to obtain reproducible results by mixing concentrated solutions of the complex ion in normal water with enriched water and precipitating the potassium salt at timed intervals, with methanol or methanol–acetone, were unsuccessful due to water in the solvents which exchanged during the precipitation process. Using $[Co(en)_3]^{3+}$ as a precipitating agent for $[Mo(O)(OH)(CN)_4]^{3-}$ was somewhat better but still was not highly reproducible due to CN^- from dissociation reacting with the Co(III) complex ion. The four procedures listed below gave consistent results all showing the oxygen to be complete at 0° in the sampling time.

A. A 50-mg sample of $K_3[Mo(O)(OH)(CN)_4]$ was placed in a sealed flask and 1.0 ml of enriched water at 0° was added. At timed intervals 200 µl of the solution was added to 10 ml of absolute ethanol containing a seed crystal. The solid was washed with absolute ethanol and ether, dried under vacuum at 150°, and converted to CO_2 as described below.

B. $K_4[Mo(O)_2(CN)_4]$ was dried at 70° under vacuum. In a sealed tube 0.763 g of this complex was added to 1.00 ml of water at 0°. At timed intervals 0.100-ml samples were taken and about 5% of the water was distilled and collected under vacuum. This water was converted to CO_2. The reaction of the dioxy complex with water to give the oxyhydroxy complex and OH^- is essentially complete and places the $[OH^-]$ at greater than 1.5 *M*.

C. To 25 ml of water containing 0.05 g of KCN at 0° was added 1.0 g of $K_3[Mo(O)(OH)(CN)_4]$ (^{18}O enriched). At timed intervals 5-ml samples were treated with 0.5 ml of a saturated $[Cr(en)_3]Cl_3$ solution at 0° and seeded, and the green crystals of $[Cr(en)_3][Mo(O)(OH)(CN)_4]\cdot H_2O$ were collected, washed with normal water and acetone, and dried under vacuum at room temperature for 12 hr. The salt was then converted to CO_2.

D. This was experimentally similar to procedure C but no cyanide ion was present.

The solid complexes and water samples were converted to pure CO_2 for isotopic measurement by heating in a sealed tube with a mixture of $HgCl_2$ and $Hg(CN)_2$ followed by purification of the gases volatile at −78° by preparative vapor-phase chromatography over silicon oil on firebrick. All operations have previously been shown not to induce exchange. Isotopic analysis was carried out on a Nuclide RMS instrument utilizing the 46/(45 + 44) ratio (R_N). A value of 4.00 × 10^{-3} was given a CO_2 standard and all reported ratios are normalized to it.

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Registry No. $[Mo(O)(OH)(CN)_4]^{3-}$, 52920-70-4; $[Mo(O)_2(CN)_4]^{4-}$, 52920-71-5.

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Magnetic Susceptibility of One-Dimensional Linear Chains of Ferromagnetically Coupled $Cu_2X_6^{2-}$ Dimers[1]

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The study of copper dimers with triplet ground states has been of much current interest.[3] In particular, it has been shown that the $Cu_2Cl_6^{2-}$ ion in $Ph_4AsCuCl_3$ existed with a triplet ground state with a singlet excited state at approximately 40 cm^{-1}.[4] The esr spectra of single crystals of the corresponding bromide salt and a mixed bromo–chloro salt are anomalous and suggest the possibility of interdimer interactions.[5] To investigate this possibility, as well as to determine the magnitude of the singlet–triplet splitting, a susceptibility study of $Ph_4AsCuBr_3$ and $Ph_4AsCuBrCl_2$ was initiated.

Experimental Section

The compounds are prepared by the slow evaporation of an aqueous solution of equimolar amounts of Ph_4AsBr and $CuBr_2$ or $CuCl_2\cdot 2H_2O$.

Table I. Molar Susceptibility

T, K	$10^4\chi_M$	T, K	$10^4\chi_M$	T, K	$10^4\chi_M$
		$Ph_4AsCuBr_3$		Ph	
4.17	2309	41.27	220	169.0	57.2
5.06	1909	46.66	219	180.7	53.1
6.22	1605	50.85	192	188.3	50.6
7.33	1364	57.33	167	201.4	48.3
7.84	1262	62.56	153	205.4	47.0
9.37	1088	67.98	140	219.4	44.2
12.10	866	72.68	127	236.6	40.1
13.62	752	77.88	118	246.0	38.2
16.20	636	80.66	114	260.0	35.9
18.43	560	121.2	85.0	267.1	35.3
23.08	456	130.2	76.6	274.5	34.4
26.91	382	138.9	71.7	295.3	32.1
31.85	314	150.0	64.4	319.0	24.7
36.75	270	160.6	60.6		
		$Ph_4AsCuBrCl_2$			
4.20	2505	23.59	465	126.0	76.3
5.84	1816	25.75	424	136.0	70.6
5.72	1852	29.03	363	148.3	64.9
6.39	1652	31.21	348	160.8	60.0
6.70	1580	34.23	313	167.6	57.0
7.57	1444	41.66	258	177.6	54.1
8.15	1341	44.95	235	186.3	50.5
9.67	1126	49.23	217	201.0	47.8
10.26	1060	53.45	200	211.8	44.8
11.37	955	58.47	181	228.5	41.0
12.41	880	62.59	168	236.4	39.7
13.85	805	66.62	156	246.3	37.9
15.35	738	70.97	145	256.8	36.5
16.08	675	76.41	131	265.5	35.2
16.85	660	79.98	123	270.8	34.1
18.28	606	84.11	117	283.6	32.0
19.65	563	117.7	82.2	291.0	31.4
21.56	508				

Crystal X-Ray analysis showed that the deep purple crystals of both compounds are isomorphous with the corresponding chlorides and gave no evidence of a supercell structure. Major constituent analyses were performed by Chemalytic, Inc., of Tempe, Ariz. *Anal.* Calcd for $Ph_4AsCuBr_3$: C, 41.73; H, 2.92; Cu, 9.25; Br, 34.70. Found: C, 41.73; H, 2.85; Cu, 9.06; Br, 34.40. Calcd for $Ph_4AsCuBrCl_2$: C, 44.61; H, 3.12; Cu, 10.63; Cl, 5.48; Br, 24.73. Found: C, 44.84; H, 3.22; Cu, 10.74; Cl, 5.64; Br, 24.84.

The Faraday technique[6] was used for magnetic susceptibility measurements in the temperature region from 78 to 300 K. Susceptibilities in the temperature range 4.2–78 K were measured utilizing the inital susceptibility technique.[7] In both cases, data were collected on polycrystalline samples obtained by grinding up single-crystal specimens. The data are tabulated in Table I.

Results

The crystal structure of $Ph_4AsCuCl_3$ contains isolated $Cu_2Cl_6^{2-}$ dimers, with dimers well separated by the Ph_4As^+ cations except along the *c* axis where the shortest Cl–Cl distance was 6.7 Å.[8] This had no apparent effect on the magnetic properties, which were readily interpreted in terms of an isolated dimer with a triplet ground state and a singlet excited state.[9] For $Ph_4AsCuBr_3$ and $Ph_4AsCuBrCl_2$, preliminary plots of $1/\chi$ *vs.* T indicated that a similar analysis might be valid. However, the plots of χT *vs.* T, shown in Figure 1, reveal more complex behavior in these cases. At high temperature, the plots extrapolate to Curie constants consistent with equal populations of the singlet and triplet levels ($C = {}^3/_4C_{\text{triplet}}$). As the temperature is lowered, the apparent Curie constants increase as the systems depopulate into the lower energy triplet states. However, instead of extrapolating to the expected value, C_{triplet}, the apparent Curie constants start to drop rapidly below 20 K.

Two possible explanations for this behavior were explored. One involves the assumption that the ground state possesses a large zero field splitting with the $M_s = \pm 1$ levels lying an energy, D, above the $M_s = 0$ level. The appropriate Ham-