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PREPARATIONS AND STRUCTURES OF (π-$C_5H_5)_2NbI_2$ AND (π-$C_5H_5)_2NbI_3$

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SUMMARY

Dicyclopentadienylniobium triiodide can be synthesized by halide ion exchange reaction from (π-$C_5H_5)_2NbCl_2OH$ and NH_4I in aqueous solution. This compound, in contrast to the other known (π-$C_5H_5)_2NbX_3$ compounds (X = Cl, Br), shows no tendency to hydrolyze. It can be crystallized as thin violet plates from dichloromethane. Dicyclopentadienylniobium diiodide is formed when (π-$C_5H_5)_2NbCl_2OH$ is reduced by benzyl mercaptan in a methanol/benzene solution, in the presence of NH_4I. This compound forms black, lustrous crystals, which are slightly air sensitive, though the compound itself is decomposed rapidly by air in solution. The compound is paramagnetic.

The infrared spectrum of (π-$C_5H_5)_2NbI_2$ is almost identical with the spectrum of the analogous zirconium compound, suggesting similar structures. The infrared spectrum of (π-$C_5H_5)_2NbI_3$ supports a structure involving parallel or near parallel cyclopentadienyl rings. Models for such a system are proposed which strongly support this structure.

INTRODUCTION

Birmingham and Wilkinson[1] reported in 1954 the synthesis of two dicyclopentadienylniobium(V) compounds, (π-$C_5H_5)_2NbBr_3$ and (π-$C_5H_5)_2NbBr_2OH$. Attempts to reduce these compounds electrochemically led to solutions of some unstable niobium complex, presumably in a lower oxidation state. This compound decomposed in solution within several minutes and could not be isolated. Subsequent to this work a patent appeared[2] which reported the two dicyclopentadienylniobium(V) chloride complexes analogous to those of Birmingham and Wilkinson. In addition poorly characterized complexes of the formulas (π-$C_5H_5)_2NbX_2$ and (π-$C_5H_5)_2NbXOH$ were described in this work. There is a brief report of a poorly characterized (π-$C_5H_5)_2Nb^{IV}$ complex having the formula (π-$C_5H_5)_2NbClBH_4$[3].

We wish to describe herein the niobium complexes (π-$C_5H_5)_2NbI_3$ and (π-$C_5H_5)_2NbI_2$. These compounds can be obtained as relatively stable entities in halogen exchange reactions with (π-$C_5H_5)_2NbCl_2OH$ and a dicyclopentadienylniobium(IV) species, respectively, the latter product being generated *in situ* from (π-$C_5H_5)_2NbCl_2OH$ and a reducing agent.

EXPERIMENTAL

Dicyclopentadienylniobium dichloride hydroxide was prepared from niobium pentachloride and sodium cyclopentadienide by the method of Wilkinson and Birmingham[1], except that its yield was maximized by intentional hydrolysis of the reaction mixture. IR spectra were obtained on a Beckman IR-10 and UV spectra were run on a Cary-14 spectrometer. Molecular weights were determined by a vapor pressure osmometer, using approximately 0.02 molal benzene solutions.

Analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

Preparation of $(\pi\text{-}C_5H_5)_2NbI_3$

A 15.0 g (103 mmoles) portion of NH_4I was added to 3.0 g (9.65 mmoles) $(\pi\text{-}C_5H_5)_2NbCl_2OH$ in a 100 ml round bottom flask and slurried with 30 ml concentrated HCl solution. The flask was stoppered and stirred intermittently for 24 h at room temperature during which time a black precipitate formed. Water and HCl were removed under vacuum and efforts were made to remove as much moisture as possible. The product was extracted using a soxhlet apparatus with 150 ml dichloromethane. During an extraction period of 40 h flat black crystals separated. The crystals were filtered and washed with 3–20 ml portions of dichloromethane, dried under nitrogen and stored in a closed vial under an atmosphere of nitrogen (1.9272 g, 33.1% yield, m.p., >300°). (Found: C, 19.63; H, 1.62; I, 62.72; Nb, 15.17, mol. wt., 590. $C_{10}H_{10}I_3Nb$ calcd.: C, 19.89; H, 1.67; I, 63.05; Nb, 15.39%; mol. wt., 604.)

IR spectrum (nujol and fluorolube mulls): 3060 vw, 1440 m, 1425 m, 1120 vw, 1060 vw, 1020 w, 1000 w, 840 s, 715 s(br), 570 w. UV spectrum (95% ethanol): 3660 Å ($\varepsilon = 8.20 \times 10^3$).

Preparation of $(\pi\text{-}C_5H_5)_2NbI_2$

A solution of 1.000 g (3.215 mmoles) $(\pi\text{-}C_5H_5)_2NbCl_2OH$, 6 ml benzyl mercaptan, 1.000 g (6.9 mmoles) NH_4I in 250 ml methanol and 150 ml benzene was prepared and allowed to stand at 25° for 20 h during which time the color changed from yellow to dark red. The solvent was removed by evaporation under vacuum, and then 500 ml toluene was added. The total volume of toluene was reduced to ~100 ml. The solvent removal was accompanied by formation of a lavender precipitate. After a second addition of toluene was followed by evaporation, this precipitate removed by filtration and discarded. The dark red crystalline product precipitated as the remainder of the toluene was removed under vacuum. The crystals were filtered and washed with two 5 ml portions of benzene and a 20 ml portion of 60–68° petroleum ether. The product was purified by dissolving it in a solution of 500 ml benzene containing 5 ml benzyl mercaptan, and allowing it to crystallize from solution by removal of all the benzene. The presence of the benzyl mercaptan seems essential for preventing product decomposition when it is in solution [0.2871 g, 18.7% yield, m.p. 155° (dec.)]. (Found: C, 25.76; H, 2.09; I, 52.39; Nb, 20.75; mol. wt., 460. $C_{10}H_{10}I_2Nb$ calcd.: C, 25.18; H, 2.12; I, 53.22; Nb, 19.48%; mol. wt., 477.)

IR spectrum (nujol and fluorolube mulls): 3090 m, 1430 m, 1115 vw, 1060 vw, 1010 m, 1000 m, 857 m, 810 s. UV spectrum (95% ethanol): 5170 Å ($\varepsilon = 9.51 \times 10^2$), 3640 Å ($\varepsilon = 7.72 \times 10^3$), 2920 Å ($\varepsilon = 1.25 \times 10^4$).

This compound was shown to be paramagnetic by Gouy balance measurements, with a magnetic moment of 1.80 B.M.

DISCUSSION

Both $(\pi\text{-}C_5H_5)_2NbI_3$ and $(\pi\text{-}C_5H_5)_2NbI_2$ could be isolated as stable crystalline substances. It is interesting that $(\pi\text{-}C_5H_5)_2NbI_3$ was prepared in a medium containing water, and that the compound itself shows no tendency to hydrolyze. Both the analogous trichloride and tribromide complexes are rapidly hydrolyzed[1,2], first to $(\pi\text{-}C_5H_5)_2NbX_2OH$ complexes, and then more slowly with complete degradation. Because of its hydrolytic stability $(\pi\text{-}C_5H_5)_2NbI_3$ is a useful starting material for further studies in this area.

Dicyclopentadienylniobium diiodide is the first well characterized $(\pi\text{-}C_5H_5)_2Nb^{IV}$ complex to be described in the literature. It is also hydrolytically stable. In solution it is rather sensitive to oxidation but as a solid it is only slightly air sensitive and can be handled without extra precautions. The formation of a niobium(IV) complex by reduction of a niobium(V) compound with a mercaptan is unique. Mercaptans are not notably strong reducing agents and this suggests that $(\pi\text{-}C_5H_5)_2Nb$ complexes in lower oxidation states than (+V) should be more easily accessible than one would be led to believe by the paucity of reported research in this area. It may be that the major problem in isolation of such complexes prior to our work is hydrolytic rather than oxidative instability of the lower oxidation state complex. This being so, it is logical that the iodide complex $(\pi\text{-}C_5H_5)_2NbI_2$ would be most likely to have a stable existence.

It is interesting to note that if air is bubbled through a liquid mercaptan containing a small amount of $(\pi\text{-}C_5H_5)_2NbI_2$ one can get rapid conversion of the mercaptan to a disulfide. Actually we made use of this property in crystallization of this compound from benzene containing a small amount of mercaptan. With mercaptan present there was no need to employ extensive techniques to avoid contact with air.

It seems likely that $(\pi\text{-}C_5H_5)_2NbI_2$ may have use as a catalyst in other types of oxidation reactions of commercial importance.

The infrared spectra of $(\pi\text{-}C_5H_5)_2NbI_2$ and $(\pi\text{-}C_5H_5)_2ZrX_2$ (X = Cl, Br)[4] are very similar, which suggests that the molecular structures of these two complexes are the same. This implies an overall geometry of $(\pi\text{-}C_5H_5)_2NbI_2$ having canted cyclopentadienyl rings, with the iodine atoms at an angle dictated primarily by Van der Waals radii and Nb–I bond distances. The structural features predicted for this compound thus parallels the features of all other $(\pi\text{-}C_5H_5)_2MX_2$ system for which structures are accurately known by X-ray crystallographic work, such as $(\pi\text{-}C_5H_5)_2Ti(SC_6H_5)_2$[5], $(\pi\text{-}C_5H_5)_2TiCl_2Al(C_2H_5)_2$[6], and $(\pi\text{-}C_5H_5)_2MoH_2$[7]. It is interesting to note, however, that assuming the structure is correct we must conclude that the extra electron in $(\pi\text{-}C_5H_5)_2NbI_2$, above that number present in the analogous zirconium complex, must not be sterically active. If this single electron was in a distinct coordination position then it is reasonable to assume that a marked deviation from the predicted geometry would be necessary, and that the structure of $(\pi\text{-}C_5H_5)_2NbI_2$ might resemble the structure of a $(\pi\text{-}C_5H_5)_2MX_3$ derivative (*vide infra*) in which one of the X groups is replaced by half of a pair of electrons. For the compounds $(\pi\text{-}C_5H_5)_2WX_2$ there is an additional electron over the niobium system; the electron pair in this compound would again appear to be inactive sterically by virtue of the observed infrared spectra[8].

The fact that $(\pi\text{-}C_5H_5)_2NbI_2$ is paramagnetic should also be noted. Many

Nb^{IV} halide complexes are now known to be diamagnetic[9] owing to spin pairing arising through metal–metal interactions in the crystal lattice. The structure of NbI_4[10] has been determined to support this picture. However, it seems likely that the predicted geometry of $(\pi\text{-}C_5H_5)_2NbI_2$ would preclude molecular packing in the solid state to allow such an interaction.

The structure of $(\pi\text{-}C_5H_5)_2NbI_3$ cannot as easily be defined however, since the only evidences bearing on structures of $(\pi\text{-}C_5H_5)_2MX_3$ compounds are conflicting and inconclusive. A canted ring structure for such systems is most often proposed based on the observed A_2B proton resonance in the NMR spectra of $(\pi\text{-}C_5H_5)_2MH_3^{n+}$ complexes ($M=W$, $n=1$; $M=Ta$, $n=0$)[11], and on a theoretical justification of this geometry[12]. However, this is not in accord with the infrared data for such systems[13]. The simplicity of the absorptions due to the $(\pi\text{-}C_5H_5)_2M$ deformation modes, and the single M–H observed stretching frequency, are more in accord with a structure involving parallel rings. Of course no X-ray crystallographic data is yet available on any complexes of this stoichiometry.

The infrared data for $(\pi\text{-}C_5H_5)_2NbI_3$ is consistent with that observed for other $(\pi\text{-}C_5H_5)_2MX_3$ systems. Thus we observed a single strong peak near 800 cm^{-1} rather than a medium intensity doublet expected for a canted ring geometry. The very weak 1000 cm^{-1} peaks were also in accord with a parallel ring structure.

Though this compound was crystalline the crystals were unsatisfactory for X-ray crystallographic studies because they could be obtained only as microscopically thin plates. Intuitively it seems that such a crystal form would be more likely to arise with molecules having the parallel ring structure.

Lacking further experimental evidence to resolve this structural problem, we chose instead to try to construct models to represent each of the possible structures. There are no available scale models of the standard types to represent niobium with nine-coordination, however. Instead we decided that the most useful procedure would be to use projection drawings of the molecule to as accurate a scale as possible. In order to do this we had to establish two things. First, we needed some rules defining the expected geometry of a canted ring system, and some criteria with which a differentiation of the two possible structures could be made. Second, we need a set of dimensions with which to work in constructing both possible structures.

It is important to consider first the three $(\pi\text{-}C_5H_5)_2MX_2$ structures[5-7] for which X-ray data have been obtained, from which these two features emerge. First the two X atoms, for example the S atoms in $(\pi\text{-}C_5H_5)_2Ti(SC_6H_5)_2$[5], are at twice the sulfur Van der Waals distance of each other, so that knowing the M–X and X–X distances the X–M–X angle is defined precisely. Second, it also happens that the hydrogen atoms closest to each other on adjacent rings in each molecule are in Van der Waals contact. It is a direct result of this that $d(M\text{–}C_5H_5)$ is a minimum. Any other $\pi\text{-}C_5H_5\text{–}M\text{–}C_5H_5$ angle (we assumed here a symmetric metal ring interaction to each carbon) will lead to a longer $d(M\text{–}C_5H_5)$ value than the one found.

These features of $(\pi\text{-}C_5H_5)_2MX_2$ can be used to predict structures of $(\pi\text{-}C_5H_5)_2MX_3$ compounds in a canted ring configuration. The MX_3 atoms would be expected to define a plane, with XMX angles well defined by Van der Waals and covalent bond distances. Moreover it seems reasonable to assume that a structure allowing the C_5H_5–M distance to be a minimum would also be most satisfactory.

The choice of metal covalent radii or bonding distances is less straightforward, for certainly these distances will vary with the nature of the complex. This would be the case for the M–C_5H_5 distance in which a multiple (and variable) interaction between metal and ring is assumed. This dimension would then be dependent on the type of complex. Lacking any definitive value from crystallographic studies of $(\pi\text{-}C_5H_5)_2Nb^V$ complexes we can only estimate a covalent radius for niobium in this complex, and assume that in comparison of the two possible structures for $(\pi\text{-}C_5H_5)_2NbI_3$ that the errors will have no effect on the gross comparison. We chose to look at M–Cl distances in several similar halides and to utilize differences between one metal and another as being primarily related to the metal radius*. On this basis we predicted a Nb covalent radius of 1.5 Å and Nb–C_5H_5 and Nb–I distances of about 2.1 Å, and 2.9 Å, respectively.

On attempting to construct the two models of $(\pi\text{-}C_5H_5)_2NbI_3$ (Fig. 1) two interesting features arose which convinced us that a parallel or near parallel ring structure was the more probable one. First utilizing the predicted d(Nb–I) distance and the standard Van der Waals radius for iodine, it turned out that the large iodine

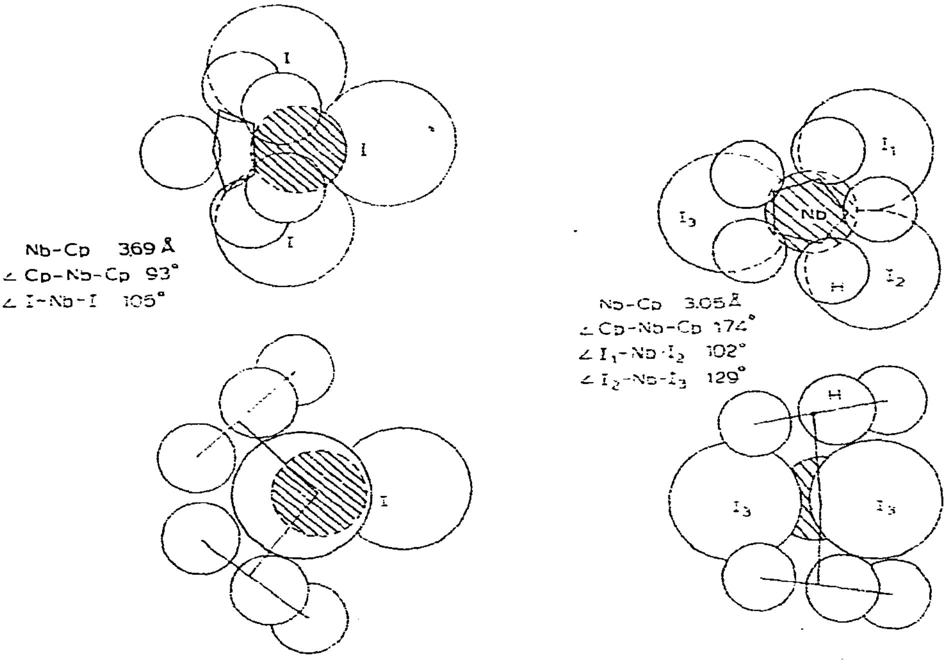

Fig. 1. (A) (B)

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* The following M–Cl bond lengths should be noted[14]: $TiCl_4$ (2.20 Å), $ZrCl_4$ (2.33 Å), $VOCl_3$ (2.12 Å), CrO_2Cl_2 (2.12 Å), $NbCl_5$ (2.29 Å) MoO_2Cl_2 (2.29 Å). The M–Cl dimensions are consistent among themselves even considering the diversity of complexes (though all were d^0), in that there is a variation in length of the M–Cl bond as anticipated for a decrease in the metal radius. If one substracts 0.99 Å, the standard chlorine covalent radius, then the resultant dimension associated with the metal radius turns out to be too small, consistently, by about 0.2 Å. [For example r(Ti) calculated on this basis would be 1.21 Å; from this: d(Ti–S) calcd.: 2.25, found 2.39, 2.42 Å; d(Ti–C_5H_5) calcd.: 1.8 Å; found 2.07 Å, in $(\pi\text{-}C_5H_5)_2$ $Ti(SC_6H_5)_2$[5].] For this reason we have chosen r(Nb) 1.50 Å, or about 0.2 Å greater than d(Nb–Cl) – r(Cl).

atoms circumscribed almost 2/3 of the circumference of the niobium atom. This overall feature was affected only slightly even if the value of d(Nb–I) was varied considerably. With this feature it was simply inappropriate to consider a canted ring structure. In order to have such a structure the value of $d(\text{M–C}_5\text{H}_5)$ would need to be 3.6 Å, a full 0.6 Å longer than necessary for the parallel ring structure.

We feel that these two points, first, the circumference of the niobium atom proscribed by the iodine ligands, and second the restrictively long value for $d(\text{M–C}_5\text{H}_5)$, offer additional support to the parallel ring structure. Admittedly our chosen model is a crude one. There are certain to be small inaccuracies in bond lengths postulated. Moreover the atom should be considered potentially able to crowd together so that the criterion involving Van der Waals radius shouldn't strictly hold. This is evident from the calculated value of 3.0 Å for $d(\text{Nb–C}_5\text{H}_5)$ which is probably longer than actually occurs. It must be stressed however that these features will not change the overall argument, favoring one structure over another.

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REFERENCES

1 G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 76 (1954) 4281.
2 J. C. Brantley, *U.S. Patent*, 2, 921, 948; *Chem. Abstr.*, 54 (1960) 11048.
3 R. B. King, *Z. Naturforsch.*, *B*, 18 (1963) 157.
4 H. P. Fritz, in F. G. A. Stone and R. West (Eds.), *Advan. Organometal. Chem.*, Vol. 1 Academic Press, New York, 1964.
5 S. Watkins, Ph.D. Thesis, University of Wisconsin, 1967.
6 G. Natta, P. Corradini and I. W. Bassi, *J. Amer. Chem. Soc.*, 80 (1958) 755.
7 M. Gerlach and R. Mason, *J. Chem. Soc.*, (1965) 296.
8 R. L. Cooper, M. L. H. Green and J. T. Moelwyn-Hughes, *J. Organometal. Chem.*, 3 (1965) 261.
9 B. N. Figgis and J. Lewis, in F. G. A. Cotton (Ed.), *Progr. Inorg. Chem.*, Vol. 6, Interscience, New York, 1964.
10 L. F. Dahl and D. Wampler, *Acta Crystallogr.*, 15 (1962) 903.
11 M. L. H. Green, J. A. McCleverty, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 4854.
12 C. J. Ballhausen and J. P. Dahl, *Acta Chim. Scand.*, 15 (1961) 1333.
13 H. P. Fritz, Y. Hristidu, H. Hummel and R. Schneider, *Z. Naturforsch.*, *B*, 15 (1960) 419.
14 A. D. Mitchell and L. C. Cross, *Interatomic Distances*, (1958) and *Supplement*, (1965), The Chemical Society, London.