reduced with lithium aluminum hydride to yield the hitherto undescribed lanostane-3β,11β,18-triol (XVI, $C_{30}H_{54}O_3$, mp 228–229°, $[\alpha]_D$ +43°). An authentic specimen of XVI was prepared as follows.

Oxidation of 3β-acetoxylanostan-11β-ol (XVII)[11] with lead tetraacetate and iodine in cyclohexane solution under illumination[12] yielded a complex mixure, which was directly reduced with lithium aluminum hydride and then subjected to successive column and thin layer chromatography to yield, after acetylation, a mixture of 11,18 (XVIII) and 11,19[12] ethers. Chromium trioxide oxidation of this mixture followed by chromatography led in 21% yield to the 11,18-lactone XIX ($C_{32}H_{52}O_4$, mp 222–222.5°, $\nu_{\max}^{\mathrm{CHCl_3}}$ 1760 and 1735 cm^{-1}), which upon reduction with lithium aluminum hydride afforded the triol XVI (mp 227–229°, $[\alpha]_D$ +43°). Identity with the sample derived from seychellogenin (III) was established by mixture melting point determination, identity of the nmr, mass, and infrared spectra, as well as identical tlc mobility. The present correlation of seychellogenin (III) with lanosterol establishes rigorously all structural and stereochemical features of the three holothurinogenins I II, and III with the exception of the stereochemistry at C-20.

[12] We employed a modification of the procedure of D. H. R. Barton, R. P. Budhiraja, and J. F. McGhie, *J. Chem. Soc., C*, 336 (1969), who recorded the isolation of one ether to which the structure of 11β,19-oxylanostan-3β-ol was assigned.

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Five-Coordinate Nickel(III). The Structure of $NiBr_3(P(CH_3)_2(C_6H_5))_2 \cdot 0.5NiBr_2(P(CH_3)_2(C_6H_5))_2 \cdot C_6H_6$

Sir:

Examples are known where a nickel complex contains either two different stereochemical arrangements for a fixed coordination number[1] *or* two different coordination numbers.[2] This communication adds a third possibility and reports the X-ray structural determination of a compound that contains simultaneously two different *oxidation states* of nickel, two coordination numbers, and two unrelated stereochemistries. In so doing it provides the first details of the stereochemistry of a Ni(III) complex.

Although trivalent nickel has been proposed in complexes with a variety of donor atoms,[3,4] evidence for the d^7 configuration is largely limited to the observation of magnetic moments in the range 1.7–2.1 BM, consistent with low-spin Ni(III).[5] On the basis of a zero dipole moment and μ_{eff} = 1.91 BM, Jensen, *et al.*,[6] reformulated $NiBr_3(P(C_2H_5)_3)_2$ as trigonal-bipyramidal rather than square-pyramidal Ni(III), as they had suggested earlier.[7] Van Hecke and Horrocks[8] observed esr signals on powdered samples of $NiBr_3((C_6H_5)_2P(CH_2)_nP(C_6H_5)_2)$ (n = 2, 3), but they were unable to interpret the electronic spectra in terms of a five-coordinate complex. Gray and coworkers[9,10] have recently questioned the representation of $[Ni(mnt)_2]^-$ and $[Ni(diars)_2Cl_2]^+$ (mnt^{2-} and diars are $(CN)_2C_2S_2{}^{2-}$ and $o\text{-}C_6H_4(As(CH_3)_2)_2$, respectively) as Ni(III) complexes, so obviously additional data are needed to substantiate the existence of trivalent nickel in molecular complexes.

Measurements on the position of equilibrium between four- and five-coordinate nickel(II) complexes led us to anticipate that pentacoordination might also be achieved by oxidation of the square-planar $NiBr_2(P(CH_3)_2(C_6H_5))_2$.[11] In fact, adding a benzene solution of bromine to a dark red solution of $NiBr_2(P(CH_3)_2(C_6H_5))_2$ gives an intensely blue solution from which we isolated a bluish black crystalline solid whose elemental analysis corresponds to the formulation $NiBr_3(P(CH_3)_2(C_6H_5))_2$ (I). *Anal.* Calcd for $C_{16}H_{22}Br_3NiP_2$: C, 33.40; H, 3.86; Br, 41.73; P, 10.80; Ni, 10.22. Found: C, 33.58; H, 3.94; Br, 41.96, 41.19; P, 10.78; Ni, 10.55. Although the solid is stable in air, solutions of I decompose slowly, thereby hindering the physical measurements, but the qualitative values indicate that I is a nonelectrolyte in nitromethane and a monomer in chloroform. The magnetic moment (μ_{eff} = 2.17 BM at 296°K) falls within the range expected for low-spin, pentacoordinate d^7 complexes.[5] In dichloromethane solutions, electronic absorption maxima have been recorded at 17,000, 20,800, 25,600, 30,300, and 37,000 cm^{-1} with ϵ values in the 3800–13,000 range. The spectrum of I in the solid state is very similar to the solution spectrum. An assignment of the spectra appears to be consistent with that expected for a Ni(III) complex and will be reported with those of other $NiBr_3L_2$ complexes.

Attempts to obtain crystals of I for a structure determination led to isolation of suitable crystals from a benzene–hexane solution. The material was found to crystallize in space group $C_i{}^1\text{-}P\bar{1}$ of the triclinic system, in a unit cell of dimensions a = 9.021 (5), b = 17.951 (10), c = 11.181 (6) Å; α = 98° 52 (1)′, β = 94° 29 (1)′, and γ = 90° 44 (1)′. The observed density of 1.67 ± 0.02 g/cm³ corresponds to 3.1 molecules of I in the cell. Since this would require one molecule of I to have a center of symmetry, further measurements were made on the recrystallized sample. The magnetic susceptibility and electronic spectra of this recrystallized sample, II, suggested a stoichiometric ratio of one diamagnetic $NiBr_2(P(CH_3)_2(C_6H_5))_2$ molecule for every two paramagnetic molecules of I. The X-ray structure determined using diffractometer data subsequently confirmed the existence of the 1:2 stoichiometry, in addition to the presence of two molecules of solvent benzene, and resulted in the first structural determination of an authentic Ni(III) complex.

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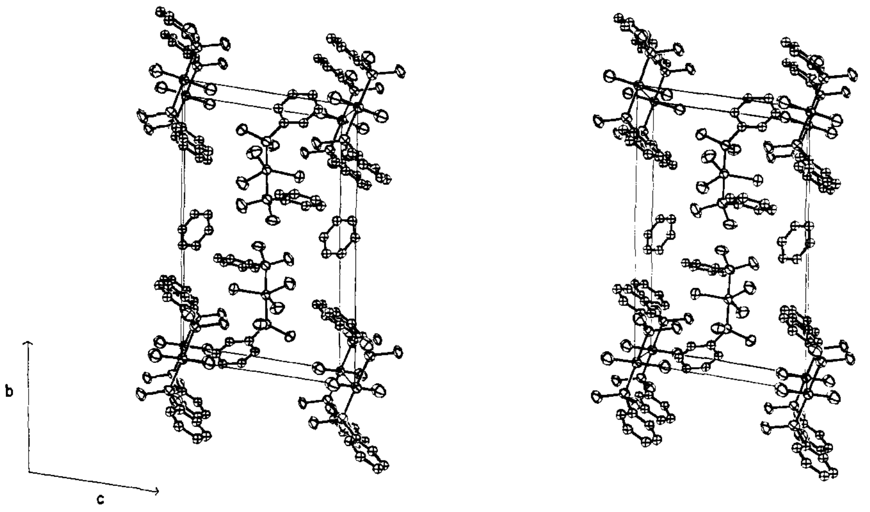

Figure 1. A stereoscopic view of the unit cell of $NiBr_3(P(CH_3)_2(C_6H_5))_2 \cdot 0.5NiBr_2(P(CH_3)_2(C_6H_5))_2 \cdot C_6H_6$. Here and in Figure 2 hydrogen atoms have been omitted for the sake of clarity.

The collection of the X-ray data and the solution and refinement of the structure were carried out by standard methods. The conventional R factor for the 2514 intensities above background is 5.4%. The highest peak on a final difference Fourier map is 1.1 e/Å^3, approximately 30% of the height of a carbon atom in this compound.

The structure consists of well-separated four- and five-coordinate molecules, with no indications of intermolecular association *via* bromide bridges (Figure 1). The *trans* square-planar molecule, $NiBr_2(P(CH_3)_2(C_6H_5))_2$, is crystallographically required to possess a center of symmetry. The Ni–P and Ni–Br bond lengths of 2.251 (3) and 2.297 (2) Å, respectively, appear to be normal for Ni(II) square-planar complexes. The P–Ni–Br angle is 90.45 (8)°.

The five-coordinate $NiBr_3(P(CH_3)_2(C_6H_5))_2$ molecule has a trigonal-bipyramidal geometry, with the two phosphines occupying the axial positions and the three bromines in the equatorial plane. The Ni and three Br atoms are coplanar, and the P–Ni–P linkage is nearly linear (178.8 (1)°). This geometry is illustrated in Figure 2; selected bond distances are also presented. There is a significant distortion from idealized trigonal-bipyramidal geometry; the Ni_2–Br_3 bond length of 2.375 (2) Å is longer than the other two distances of 2.339 (2) and 2.349 (2) Å, and the angle opposite this long bond is expanded to 132.71 (9)° from the expected 120°. The complex contains Ni(III) in a low-spin d^7 electronic configuration and is subject to Jahn–Teller considerations which should remove the degeneracy of the d_{xy} and $d_{x^2-y^2}$ orbitals in D_{3h} symmetry, resulting in the observed geometry.

We have examined esr spectra of both I and II as solids at room temperature and in a frozen toluene solution at 77°K. The absence of a resonance is evidence against an assignment of these complexes as "metal-stabilized radical–ligand" systems[9,10] since an anisotropic pattern with $\langle g \rangle$ values near 2.0–2.1 would be expected.[4,9,10] For a Ni(III) formulation, the predicted anisotropic g values may not be observed because of the short spin-lattice relaxation time of the pentacoordinate system.[12] The measured magnetic moment of II was 1.71 BM per nickel. By considering that one-third of the molecules are diamagnetic, the recalculated magnetic moment is 2.09 BM per Ni(III) ion, in good agreement with the value obtained originally on I.

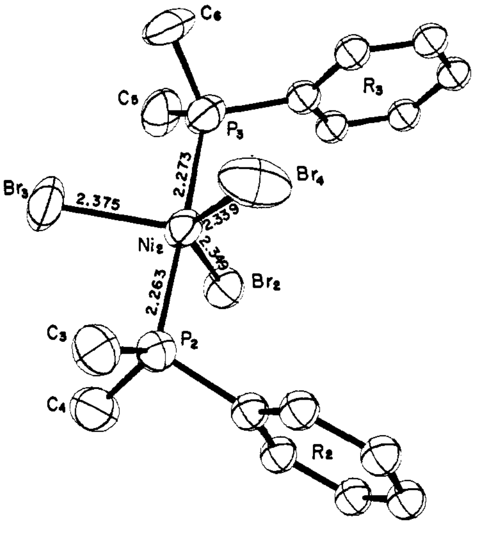

Figure 2. A perspective drawing of $NiBr_3(P(CH_3)_2(C_6H_5))_2$.

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Photochemical and γ-Ray-Induced Reactions of Purines and Purine Nucleosides with 2-Propanol

Sir:

The photochemical reactions of purine and alcohols as well as the radiation- and ultraviolet-induced reac-