by addition of a 1:1 mixture of petroleum ether and ethyl ether; yield 75%. The infrared spectrum is reported in Table I.

$[Pt(PPh_3)_2(SPh)_2PdCl_2]$. Equimolar amounts of $[Pt(PPh_3)_2(SPh)_2]$ and $(CH_3CN)_2PdCl_2$ reacted in benzene for 6 hr. Concentration of the solution at reduced pressure and addition of ethyl ether to the resulting solution gave a yellow solid; yield 80%. Infrared spectrum (Nujol mull): ν(Pd–Cl) 318 (s), 330 (sh), 324 (sh), 306 (sh), 295 cm^{-1}. Mol wt in $CHCl_3$: calcd, 1115; found, 1036.

Palladium Complexes. All the complexes were prepared by the same procedures as those used for the analogous platinum derivatives: **$[Pd(PPh_3)(SPh)_2]_2$**: yield 85%; reaction time 10 hr. Mol wt in C_6H_6: calcd, 1174; found, 1130. **$[Pd(PPh_3)_2(o\text{-}O_2NC_6H_4S)_2]$**: yield 80%; reaction time 2 hr. Infrared spectrum (Nujol mull): $\nu(NO_2)$ 1502, 1326 cm^{-1}. Mol wt in C_6H_6: calcd, 939; found, 890. **$[Pd(PPh_3)_2(m\text{-}O_2NC_6H_4S)_2]$**: yield 70%; reaction time 2 hr. Infrared spectrum (Nujol mull): $\nu(NO_2)$ 1518, 1345 cm^{-1}. Mol wt in C_6H_6: calcd, 939; found, 915. **$[Pd(PPh_3)_2(NCS)_2]$**: yield 70%; reaction time 4 hr. Infrared spectrum (Nujol mull): ν(CN) 2090 cm^{-1}, ν(CS) 845 cm^{-1}.

$[Pd(PPh_3)(SPh)I]_2$. A benzene solution of $[Pd(PPh_3)(SPh)_2]_2$ reacted with an excess of CH_3I for 12 hr at room temperature. The resulting solution was concentrated at reduced pressure and addition of a 1:1 mixture of ethyl ether and petroleum ether produced a red solid, which was collected on a filter, washed with the same solvent, and dried under vacuum; yield 80%. In the mother liquor, analyzed by glc using a Chromosorb column, was detected $PhSCH_3$.

Reactions with HCl. In a typical experiment a benzene solution of $[Pt(PPh_3)_2(SPh)_2]$ reacted with hydrogen chloride for a few minutes. *cis*-$[Pt(PPh_3)_2Cl_2]$ was formed. Glc analysis of the solution on a Chromosorb column showed the presence of PhSH.

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Registry No. $[Pt(PPh_3)_2(PhS)_2]$, 31168-85-1; $[Pt(PPh_3)_2(m\text{-}NO_2C_6H_4S)_2]$, 41507-74-8; $[Pt(PPh_3)_2(o\text{-}NO_2C_6H_4S)_2]$, 41507-75-9; $[Pt(PPh_3)_2(NCS)_2]$, 41507-76-0; $[Pt(PPh_3)_2(PhS)_2Mo(CO)_4]$, 41499-76-7; $[Pt(PPh_3)_2(PhS)_2PdCl_2]$, 41507-77-1; $[Pd(PPh_3)(PhS)_2]_2$, 41507-78-2; $[Pd(PPh_3)_2(m\text{-}NO_2C_6H_4S)_2]$, 41507-79-3; $[Pd(PPh_3)_2(o\text{-}NO_2C_6H_4S)_2]$, 41507-80-6; $[Pd(PPh_3)_2(NCS)_2]$, 41507-81-7; $[Pd(PPh_3)(PhS)I]_2$, 41507-82-8; $[Pt(PPh_3)_4]$, 14221-02-4; PhSSPh, 882-33-7; $(SNC)_2$, 505-14-6; (norbornadiene)$Mo(CO)_4$, 12146-37-1; $(CH_3CN)_2PdCl_2$, 14592-56-4; CH_3I, 74-88-4; $[Pd(PPh_3)_4]$, 14221-01-3; HCl, 7647-01-0.

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Dioxygenyl Salts $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ and Their Convenient Laboratory Syntheses

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The first claim for the salt of formulation $O_2^+SbF_6^-$ was that of Young, *et al.*[1] These authors prepared their material by interaction of O_2F_2 with SbF_5. A puzzling feature of this report, however, was the rather large cubic unit cell quoted, for which a = 10.71 Å, since in the previously characterized[2] platinum analog a = 10.032 Å. In later papers Shamir and Binenboym described[3] a photochemical synthesis for what was claimed to be $O_2^+SbF_6^-$ and Beal, *et al.*, described[4] a preparation from SbF_5, F_2, and O_2 which simply involved heating this mixture. The first authors presented no unambiguous evidence for the formulation $O_2^+SbF_6^-$ and quoted a cubic unit cell constant of 10.30 Å, a value which, although more acceptable than that of Young, *et al.*, still seemed rather high. Beal, *et al.*, provided X-ray powder data to support a unit cell of 10.13 Å, a value in much closer harmony with the cell parameter for the cubic $O_2^+PtF_6^-$ salt.[2] The X-ray powder data of Beal, *et al.*, were, however, ascribed to a face-centered cell, whereas the full data (some of which was omitted from their tabulation) supported a body-centered cell with a = 10.13 Å. It is now clear that weak diffraction lines were omitted from their data. These represent (as discussed[2] by Bartlett and Lohmann for the $O_2^+PtF_6^-$ case) diffraction by the light atom superlattice and are of crucial structural importance.

In their differential thermal analysis of $O_2^+SbF_6^-$ Nikitina and Rosolovskii recognized[5] the existence of the $O_2^+Sb_2F_{11}^-$ salt as well as $O_2^+SbF_6^-$ and attempted a characterization of the two salts on the basis of X-ray powder data. Their data, however, are not that for the pure components $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$. Furthermore, Nikitina and Rosolovskii also failed to recognize $O_2^+SbF_6^-$ as an isomorph of $O_2^+PtF_6^-$.

Although the O_2^+ stretching frequency has been reported[6] for what was stated to be the $O_2^+SbF_6^-$ salt, the anion spectra were not given.

The X-ray powder data given in Table I and the Raman spectrum shown in Figure 1B characterize the $O_2^+SbF_6^-$ salt. The X-ray data establish that the compound is isomorphous with $O_2^+PtF_6^-$. The unit cell is cubic with $a = 10.132 \pm 0.002$ Å, V = 1040 Å^3, $Z = 8$, d_c = 3.418 g cm^{-3}. Since all observed reflections obey the conditions $h + k + l = 2n$ and $0kl$ where $k(l) = 2n$, the indicated space group is $Ia3$ (No. 206)[7] as established for O_2PtF_6.[2,8] The formula unit volume of 130 Å^3 is 2.4 Å^3 less than that found for $NO^+SbF_6^-$ by Bartlett and Jha.[9] This is comparable to the PtF_6^- case where[10] $V(NO^+PtF_6^-)$ = 129.5 Å^3 and $V(O_2^+PtF_6^-)$ = 126.3 Å^3. The close similarity of the intensities of the weak powder diffraction lines (oxygen and fluorine diffraction only), compared with those in the platinum relative,[9] suggests an isostructural relationship. Comparison of the Raman spectrum with that of $O_2^+PtF_6^-$ (given in Figure 1C) further supports the close structural similarity.

The X-ray powder data for $O_2^+Sb_2F_{11}^-$ given in Table II have not been indexed and all attempts to grow single crystals have failed. The Raman spectrum given in Figure 1A again gives clear evidence of the O_2^+ ion (in the band at 1865 cm^{-1}) and the anion spectrum shows relationship to the SbF_6^- spectrum. The anion spectrum is in fact simpler than in $XeF^+Sb_2F_{11}^-$ (ref 11) and $XeF_3^+Sb_2F_{11}^-$ (ref 12).

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Table I. X-Ray Powder Data for $O_2^+SbF_6^-$ [a]

d, Å	$1/d^2_{obsd}$	$1/d^2_{calcd}$	*hkl*	I/I_0
5.091	0.0385	0.0390	200	8
3.595	0.0772	0.0779	220	10
2.915	0.1175	0.1169	222	5
2.697	0.1371	0.1364	321	2
2.534	0.1556	0.1558	400	4
2.389	0.1751	0.1753	411	2
2.260	0.1957	0.1948	420	5
2.159	0.2144	0.2143	332	3
2.067	0.2339	0.2338	422	7
1.980	0.2550	0.2533	431	1
1.785	0.3138	0.3117	440	5
1.685	0.3520	0.3507	442, 600	5
1.597	0.3919	0.3896	620	5
1.521	0.4322	0.4286	622	5
1.461	0.4685	0.4676	444	2
1.430	0.4891	0.4871	543	<1
1.401	0.5095	0.5065	640	4
1.374	0.5294	0.5260	633, 721, 552	1
1.351	0.5480	0.5455	642	5
1.283	0.6070	0.6040	732, 651	1
1.265	0.6257	0.6234	800	1
1.226	0.6650	0.6624	820, 644	4
1.192	0.7047	0.7014	822, 660	4
1.160	0.7435	0.7403	662	3
1.131	0.7827	0.7793	840	3
1.104	0.8212	0.8182	842	3
1.077	0.8623	0.8572	664	3
1.033	0.9371	0.9351	844	2
1.012	0.9759	0.9741	10, 0, 0, 860	2
0.9926	1.015	1.013	10, 2, 0, 862	4
0.9738	1.054	1.052	10, 2, 2, 666	3
0.9396	1.132	1.130	10, 4, 0, 864	4
0.9240	1.171	1.169	10, 4, 2	3
0.8945	1.249	1.247	880	1
0.8811	1.287	1.286	10, 4, 4, 882	3
0.8681	1.326	1.325	10, 6, 0, 866	3
0.8556	1.365	1.364	10, 6, 2	3
0.8438	1.404	1.403	12, 0, 0, 884	3
0.8324	1.443	1.442	12, 2, 0	2
0.8215	1.482	1.481	12, 2, 2, 10, 6, 4	4
0.8006	1.560	1.558	12, 4, 0	2
0.7910	1.598	1.597	12, 4, 2, 10, 8, 0, 886	6
0.7816	1.637	1.636	10, 8, 2	4

[a] Cubic: $a = 10.132 \pm 0.002$ Å (cell dimension obtained from an extrapolation using the Nelson–Riley function: L. V. Azaroff and M. J. Buerger, "The Powder Method," McGraw-Hill, Toronto, 1958, p 238), $V = 1040$ Å^3, $Z = 8$, $d_c = 3.418$ g/cm^3, space group $Ia3$, Cu Kα radiation Ni filter.

Table II. X-Ray Powder Data for $O_2^+Sb_2F_{11}^-$ [a]

d, Å	$1/d^2$	I/I_0	*d*, Å	$1/d^2$	I/I_0
7.809	0.0164	1	2.824	0.1253	3
6.476	0.0238	1	2.721	0.1350	3
5.739	0.0304	2	2.622	0.1453	2
5.354	0.0349	6, br	2.520	0.1575	1
4.941	0.0410	2	2.454	0.1661	3
4.634	0.0465	1	2.131	0.2201	2
4.306	0.0539	1	2.031	0.2423	2
3.951	0.0640	10, br	1.949	0.2632	1
3.767	0.0705	1	1.882	0.2822	1
3.616	0.0765	6, br	1.791	0.3117	1
3.436	0.0847	2	1.704	0.3442	1
3.213	0.0969	1, v br	1.651	0.3665	1
2.948	0.1151	1	1.618	0.3822	3

[a] Cu Kα radiation, Ni filter.

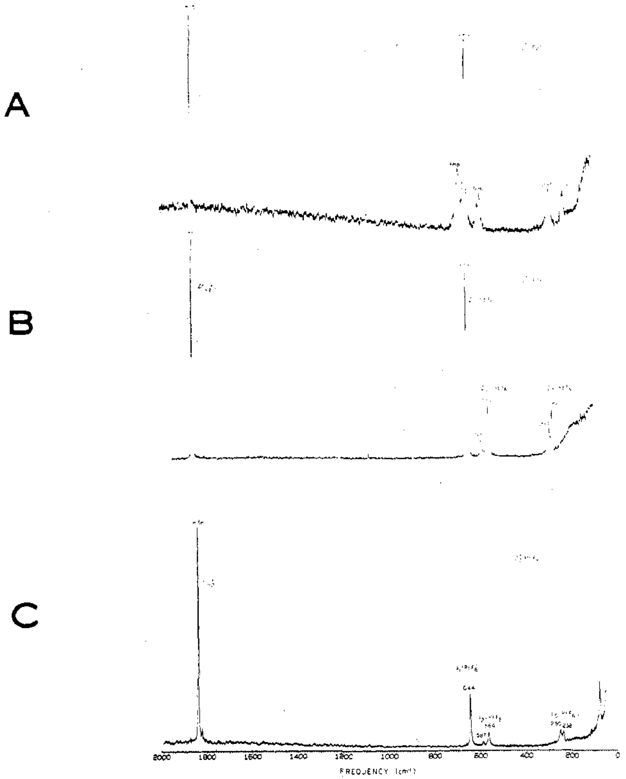

Figure 1. Raman spectra of (A) $O_2^+Sb_2F_{11}^-$; (B) $O_2^+SbF_6^-$; (C) $O_2^+PtF_6^-$.

It may be that the anion in $O_2^+Sb_2F_{11}^-$ possesses a linear bridge and that the O_2^+ species are symmetrically placed about the anion. This would account for the absence of features in the Raman spectrum attributable to bridge stretching. In the $XeF^+Sb_2F_{11}^-$ and $XeF_3^+Sb_2F_{11}^-$ salts the bridge angles are 150 (ref 13) and 155° (ref 14), respectively, and the salts show Raman bands attributable to bridge stretch at 482 (ref 11) and 487 cm^{-1} (ref 12), respectively. In $BrF_4^+Sb_2F_{11}^-$ where the bridge angle is not significantly deviant from linearity,[15] this Raman feature is not observed.[12] The presence of a band at 470 cm^{-1} in the infrared spectrum of $O_2^+Sb_2F_{11}^-$ indicates that the strength of the bridge bond on the anion is not much different from that in the other salts and, coupled with the absence of its counterpart in the Raman, argues for a linear anion.

Experimental Section

$O_2^+Sb_2F_{11}^-$ was prepared by irradiation of a fluorine, oxygen, and antimony pentafluoride mixture contained in a Pyrex bulb provided with a Kel-F tipped Whitey valve joined to the bulb through a Kovar seal. A 450-W Hanovia ultraviolet lamp was used at a distance of 6 in.; irradiations lasted 12–16 hr. A stoichiometry appropriate for the reaction $O_2 + {}^1/_2F + 2SbF_5 \rightarrow O_2Sb_2F_{11}$ was found to be best; thus, 69.0 mmol of SbF_5 with 34.5 mmol of O_2 and 17.3 mmol of F_2 in a 5-l. flask were quantitatively converted to $O_2Sb_2F_{11}$ in 12 hr. In irradiations where an excess of F_2 and O_2 over that required for $O_2Sb_2F_{11}$ formation prevailed, $O_2^+SbF_6^-$ was also observed in the product. Use of excess SbF_5 necessitated the removal of this material from the product but this approach does provide pure $O_2^+Sb_2F_{11}^-$.

O_2SbF_6 was prepared by heating $O_2Sb_2F_{11}$ in a dynamic vacuum at 110°. At that temperature, the SbF_5 is removed slowly and at an approximately constant rate. If removal of SbF_5 is halted at a weight corresponding to loss of 1 mol of SbF_5 per mole of $O_2Sb_2F_{11}$, the material which remains provides the X-ray powder pattern and the Raman spectrum assigned to $O_2^+SbF_6^-$. The $O_2^+SbF_6^-$ salt itself is unstable under those preparative conditions, but $O_2^+Sb_2F_{11}^-$ decomposes to $O_2^+SbF_6^-$ at a greater rate. It is therefore essential to monitor the rate of loss of SbF_5 so that SbF_5 removal may be halted

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when the last of the $Sb_2F_{11}^-$ salt has decomposed. The conversion of 5.55 mmol of $O_2Sb_2F_{11}$ to 5.54 mmol of O_2SbF_6 required 282 hr at 110°. $O_2Sb_2F_{11}$ may be converted to O_2SbF_6 more rapidly under vacuum at higher temperatures, but the yield is lower; *e.g.*, at 160° the conversion of 0.76 mmol of $O_2Sb_2F_{11}$ to 0.49 mmol of O_2SbF_6 was complete in only 3 hr the loss of material being due to thermal decomposition. X-Ray powder photography and Raman spectroscopy revealed that removal of SbF_5 from $O_2^+Sb_2F_{11}^-$ was associated with the appearance of $O_2^+SbF_6^-$. No phases other than $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ were indicated.

$O_2Sb_2F_{11}$ was also prepared from O_2SbF_6. The 1:1 salt (1.75 mmol) was placed in a Pyrex tube with excess SbF_5 (2–3 ml), under 300 mm of nitrogen pressure. The tube was brought to 125° and shaken. A clear solution was not obtained, but care was taken to break up the clumps of solid by agitating the mixture to a white slurry. The mixture was cooled to room temperature before unreacted SbF_5 was removed under vacuum. The white solid which remained was shown by X-ray and Raman spectra to be $O_2Sb_2F_{11}$ and the weight corresponded to 1.61 mmol.

The preparative technique for X-ray powder diffraction and Raman samples has been previously described, as has the equipment used.[12] Long exposure times were required to obtain a suitable powder pattern for $O_2^+Sb_2F_{11}^-$, but the 26 lines reported in Table II unambiguously fingerprint that compound. The Raman spectra have been intensity corrected for nonlinear sensitivity of the phototube. For the antimony salts the exciting line was the 5145-Å Ar^+ line and for the deep red platinum salt the 6741-Å Kr^+ line.

Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Perkin-Elmer 237 Infracord spectrophotometer. The powdered solids were pressed between AgCl windows in an all Kel-F cell. O_2SbF_6 shows only one broad band in the region examined, at 660–670 cm^{-1}, characteristic of the ν_3 mode of the SbF_6^- ion. $O_2Sb_2F_{11}$ shows three bands centered at 677, 652, and 470 cm^{-1}.

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Registry No. $O_2^+Sb_2F_{11}^-$, 12592-38-0; $O_2^+SbF_6^-$, 12361-66-9; SbF_5, 7783-70-2; F_2, 7782-41-4; O_2, 7782-44-7.

Correspondence

Proton Magnetic Resonance Spectra of Nickel(II)- and Cobalt(II)-1,8-Naphthyridine Complexes. A Comparison among the Contact Shift Patterns of Heterocyclic Nitrogen Ligands

Sir:

The enthusiasm of researchers in the proton contact shift field has recently attenuated owing to the lack of a simple model correlating the observed shifts to the nature of the coordinative bond in metal complexes. Theoretical models of increasing sophistication have been proposed[1-5] and laborious calculations have been performed which gained in some cases partial success[4-6] but never found general applicability. In many istances however these partial models have been the origin of lively controversies.[4-8]

The numerous investigations on nickel(II) and cobalt(II) complexes with nitrogen-containing heterocyclic ligands are typical in this connection. First, Happe and Ward[9] suggested that the spin-delocalization mechanism in pyridine complexes occurred *via* σ bonds; Holm, Everett, and Horrocks[10] proposed that also some π ligand orbitals were involved but they were unsuccessful in matching the observed contact shifts through an extended Huckel molecular orbital treatment of the pyridine anion. By mixing the two σ and π mechanisms Cramer and Drago[8] reproduced the pattern of the shifts for para-substituted pyridine ligands but failed to do it for pyridine. Finally INDO calculations reproduced the observed values but pyridine had to be treated either as a phenyl radical or as a mixture of cation and anion.[4,5]

The recent report on nickel(II) and cobalt(II) complexes with 1,8-naphthyridine (napy)[11] stimulated us to determine the isotropic shift pattern onto this ligand for the following reasons: (i) the complexes are reported to be octacoordinated with an idealized D_{2d} symmetry; (ii) the ligand is structurally similar to pyridine (py), dipyridine (dipy), and phenantroline (phen) and a comparison of the contact shifts among all these ligands may provide useful information on the spin-delocalization mechanisms.

The pmr traces of the $[M(napy)_4](ClO_4)_2$ complexes (M = Ni, Co) are reported in Figure 1 together with the assignment proposed on the basis of line width, the analogy with the spectra of pyridine complexes, and comparison with the spectra of 4-methyl-1,8-naphthyridine. By cooling the solutions the line width drastically increases indicating that there is an interconversion among different species whose rate becomes of the same order of magnitude of the nmr resonance[12] at low temperature. Molecular weight measurements on 10^{-2} *M* solutions of the nickel complex in nitromethane gave an association degree $\bar{n} = 0.36$.[13] In order to evaluate this figure, molecular weight measurements were performed on solutions containing $[Ni(dipy)_3](ClO_4)_2$ (1:2 electrolyte) and $[Ni(dipy)_3](ClO_4)_2$ with dipy added in 1:1 molar ratio. The $\bar{n}$ values obtained are 0.40 and 0.30, respectively. These data suggest that in the case of the napy complexes the following dissociation equilibrium takes place

$$[M(napy)_4]^{2+} \rightleftharpoons [M(napy)_3]^{2+} + napy$$

This equilibrium may be responsible for the observed equivalence of the two rings of napy, while two signals for each ring position would be expected on the basis of the dodecahedral structure of the complexes.[14]

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