At this temperature a mononuclear complex ($\delta(^{31}P)$ 62.2 ($^1J(^{31}P-^{195}Pt)$ = 2600 Hz)) begins to appear. When the temperature is increased to −10 °C, a second species forms that is dinuclear with two equivalent phosphine environments ($\delta(^{31}P)$ 60.9 ($^1J(^{31}P-^{195}Pt)$ = 2630 Hz, $|J(^{31}P-Pt\cdots{}^{195}Pt)|$ = 17 Hz, $|J(^{31}P-Pt\cdots{}^{31}P)|$ = 15 Hz). The product **2** forms at 0 °C. We have no other information about the nature of the two intermediates but are confident that the reaction proceeds via a mononuclear pathway. The reaction of $Pt_3(CO)_3(P(t\text{-}Bu)_3)_3$ with CS_2 is very much slower than the aforementioned examples and appears to produce a mixture of products. We are currently examining this reaction to try to elucidate the nature of the intermediates.

The reaction of $Pt(P(t\text{-}Bu)_3)_2$ with CS_2 has recently been reported.[4] Single crystals could not be obtained, and thus the complex formed was postulated as $Pt_3(CS_2)_3(P(t\text{-}Bu)_3)_3$ on the basis of analytical, IR, and molecular weight data. We prepared this complex and report the ^{31}P NMR data in Table IV. The ^{195}Pt satellite pattern unequivocally demonstrates that the complex is dimeric and, on the basis the similarity with **2**, is in fact $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$. $Pt(P(t\text{-}Bu_2)Ph)_2$ reacts with CS_2 to produce **2**. We have also found that bis(phosphine)palladium(0) complexes react with CS_2 to produce either mononuclear $Pd(\eta^2\text{-}CS_2)L_2$ or dinuclear $Pd_2(\mu\text{-}CS_2)_2L_2$ complexes (L = a phosphine ligand) depending upon the nature of the phosphine ligand.[17]

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Registry No. **2**, 91686-59-8; $Pt_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$, 91686-60-1; $Pd_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_2Ph)_2$, 91686-61-2; $Pd_2(\mu\text{-}CS_2)_2(P(t\text{-}Bu)_3)_2$, 91686-62-3; $Pt_3(CO)_3(P(t\text{-}Bu)_2Ph)_3$, 62931-81-1; $Pt_3(CO)_3(P(t\text{-}Bu)_3)_3$, 79138-89-9; $Pd_3(CO)_3(P(t\text{-}Bu)_2Ph)_3$, 62931-80-0; $Pd_3(CO)_3(P(t\text{-}Bu)_3)_3$, 62931-79-7; $Pt(P(t\text{-}Bu)_3)_2$, 60648-70-6; $Pt(P(t\text{-}Bu)_2Ph)_2$, 59765-06-9; CS_2, 75-15-0.

Supplementary Material Available: Listings of weighted least-squares plane data for $PPt(CS_2)_2PtP$ core, hydrogen atom parameters, anisotropic thermal parameters, and structure amplitudes as $10|F_o|$ vs. $10|F_c|$ (16 pages). Ordering information is given on any current masthead page.

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Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

Synthesis and Characterization of Bis[difluorooxychlorine(V)] Hexafluoronickelate(IV), $(ClF_2O)_2NiF_6$

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It is well-known that ClF_3O can form with strong Lewis acids, such as BiF_5, SbF_5, AsF_5, PF_5, TaF_5, NbF_5, VF_5, PtF_5, UF_5, SiF_4, BF_3, HF, and MoF_4O, adducts containing the ClF_2O^+ cation.[1-6] All these adducts have been prepared by the direct combination of ClF_3O with the corresponding Lewis acids. The purpose of this study was to examine whether ClF_2O^+-containing salts derived from unstable Lewis acids, such as NiF_4, can be prepared by the indirect metathetical methods developed for NF_4^+ salt chemistry.[7]

Experimental Section

Materials and Apparatus. Literature methods were used for the syntheses of Cs_2NiF_6[7] and ClF_2OSbF_6[4] and the drying of the HF solvent.[8] Volatile materials were manipulated in a well-passivated (with ClF_3) stainless-steel Teflon FEP vacuum system.[9] Solids were handled in the dry-N_2 atmosphere of a glovebox.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.[10,11] Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Spex Model 1403 spectrophotometer using the 6471-Å exciting line of a Kr ion laser and premonochromators for the elimination of plasma lines. Sealed quartz tubes were used as sample containers. The low-temperature spectra were recorded by using a previously described device.[12]

Synthesis of $(ClF_2O)_2NiF_6$. A mixture of ClF_2OSbF_6 (7.008 mmol) and Cs_2NiF_6 (3.505 mmol) was loaded in the drybox into a previously described[10] double-U-tube filter apparatus. Dry HF (185 mmol) was condensed at −196 °C into the apparatus on the vacuum line, and the mixture was warmed for 30 min to 25 °C with agitation. The apparatus was cooled to −78 °C and inverted, and the solid and liquid phases were separated by filtration assisted by 2 atm of dry N_2 gas. The material volatile at 25 °C was pumped off for 12 h and consisted mainly of HF. The filter cake (2.768 g; weight calculated for 7.01 mmol of $CsSbF_6$, 2.584 g) was shown by vibrational spectroscopy to consist of mainly $CsSbF_6$ containing small amounts of ClF_2O^+[11] and NiF_6^{2-}.[7] The filtrate residue (965 mg; weight calculated for 3.505 mmol of $(ClF_2O)_2NiF_6$, 1.232g, corresponding to a 78% yield) was shown by elemental analysis and vibrational spectroscopy to have the following composition (wt %): $(ClF_2O)_2NiF_6$, 93.04; ClF_2OSbF_6, 1.49; $CsSbF_6$, 5.47. Anal. Calcd: Ni, 15.54; Cl, 18.93; Cs, 1.97; Sb, 2.36. Found: Ni, 15.6; Cl, 18.7; Cs, 2.07; Sb, 2.48. The losses of $(ClF_2O)_2NiF_6$ can be attributed mainly to hang-up of some $(ClF_2O)_2NiF_6$ on the filter cake.

Results and Discussion

Synthesis and Properties of $(ClF_2O)_2NiF_6$. The metathetical process previously developed for $(NF_4)_2NiF_6$[7] has successfully been transferred to the synthesis of $(ClF_2O)_2NiF_6$ according to

$$2ClF_2OSbF_6 + Cs_2NiF_6 \xrightarrow[-78\ ^\circ C]{\text{HF solution}} 2CsSbF_6\downarrow + (ClF_2O)_2NiF_6$$

The new compound $(ClF_2O)_2NiF_6$ is a deep purple crystalline solid that is stable at 60 °C under a dynamic vacuum. At 110 °C the observed decomposition rate was about 25%/h. The main decomposition products, volatile at ambient temperature but condensible at −196 °C, were ClF_3O and a small amount of $FClO_2$ (arising from handling of the ClF_3O) as shown by their ^{19}F NMR and infrared spectra.[11] An exhaustive pyrolysis of a sample in a sapphire reactor at 110 °C under a dynamic vacuum resulted in quantitative ClF_3O evolution and the

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formation of a previously described[7] nonstoichiometric brown nickel fluoride $NiF_{2.x}$ residue. Contrary to the pyrolysis of $(NO)_2NiF_6$, which results in the formation of NF_3O,[13] no evidence for the formation of the unknown compound ClF_5O was observed.

The presence of ClF_2O^+ and NiF_6^{2-} ions in $(ClF_2O)_2NiF_6$ was established by vibrational spectroscopy. The spectra of the solid showed bands characteristic for ClF_2O^+ (IR, 1324 vs (ν_1), 700 vs, br (ν_2, ν_5), 502 s (ν_3), 406 m (ν_4), 376 m (ν_6))[11] and NiF_6^{2-} (IR, 625 vs (ν_3), 330 m (ν_4); Raman, 565 vs (ν_1), 525 s, 512 ms (ν_2), 308 m, 290 w (ν_5))[7] with ν_2 and ν_5 of NiF_6^{2-} showing splittings due to lifting of the degeneracies of these modes. Due to the intense color of the sample, it ws difficult to obtain Raman spectra and only the bands due to NiF_6^{2-} could be observed even at −100 °C.

Conclusion. The above results show that ClF_2O^+ salts derived from unstable Lewis acids, such as NiF_4, can be prepared by metathetical methods. Furthermore, $(ClF_2O)_2NiF_6$ is the first example of ClF_2O^+ having been coupled successfully to a highly energetic anion in the form of a stable salt.

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Registry No. $(ClF_2O)_2NiF_6$, 91443-95-7; ClF_2OSbF_6, 38199-85-8; Cs_2NiF_6, 17218-49-4.

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Dynamic Jahn-Teller Effects in High-Spin Trigonal-Bipyramidal Nickel(II) Complexes

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Trigonal-bipyramidal nickel(II) complexes have long been known to have a room-temperature magnetic moment distinctly smaller than the value that would be expected for a $^3E'$ ground state.[1,2] This has been attributed either to an admixture of an excited orbital doublet state,[3] which has a smaller M_L value as compared to that of the ground state, or to Jahn-Teller effects.[4] Recently Hempel and Miller[5] reproposed the validity of the former hypothesis on the basis of ligand field calculations, which allowed the authors to reproduce the room-temperature magnetic moment of [NiBr(Me_6tren)]Br (Me_6tren = 2,2′,2″-tris(dimethylamino)triethylamine) and to predict a value of 3.35 μ_B for the moment at 5 K.

To our knowledge no data are available in the literature relative to low-temperature magnetic susceptibility for high-spin trigonal-bipyramidal nickel(II) complexes. Since, in principle, magnetic measurements can give some information on the energies of the spin–orbit low-symmetry split components of the ground $^3E'$ level, we decided to measure the magnetic susceptibilities of [NiBr(Me_6tren)]Br and [NiNCS(Me_6tren)]SCN·H_2O. For these two complexes the crystal structures are available,[4,6] and for the latter single-crystal polarized electronic spectra have been published as well.[4]

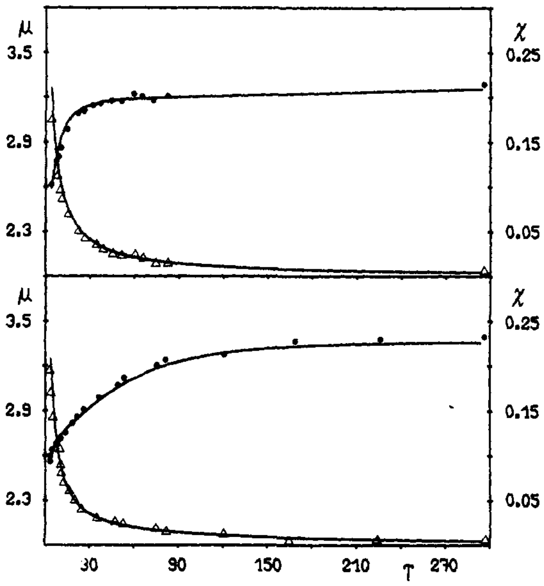

Figure 1. Observed values of magnetic moments (●) and susceptibility (△) for [NiBr(Me_6tren)]Br (bottom) and [NiNCS(Me_6tren)]NCS·H_2O (top). The curves reproduce the calculated values with the model described in the text.

Table I. Best-Fit Values of Angular Overlap Parameters for [NiBr(Me_6tren)]Br and [NiNCS(Me_6tren)]SCN·H_2O

	Br			NCS		
	r^a	e_σ	e_π	r^a	e_σ	e_π
N_{ax}	2.10	4326		2.04	4335	
N_1	2.13	4350		2.13	4270	
N_2	2.13	4350		2.08	4270	
N_3	2.13	4350		2.09	4270	
X	2.467	4800	1400	1.97	5820	1000

[a] The distance of the indicated atom to the metal ion.

The magnetic susceptibility data for the complexes were measured with two different techniques: a Faraday balance was used for [NiBr(Me_6tren)]Br and a vibrating-sample magnetometer for [NiNCS(Me_6tren)]SCN·H_2O. The temperature dependence of the magnetic susceptibility and of the effective magnetic moment of the two complexes (which agree with a paramagnetic behavior) is shown in Figure 1. The room-temperature moments are 3.30 μ_B for the thiocyanate and 3.42 μ_B for the bromide derivative. They decrease steadily until they become 2.61 μ_B for the former and 2.56 μ_B for the latter at 4.2 K, slightly below the spin-only value. These data appear to contrast with the predictions of previous theoretical treatments, which require much higher moments at low temperature.[5]

In order to interpret these data, the angular-overlap model (AOM) was used in the form first suggested by Gerloch.[7] The e_λ ($\lambda = \sigma, \pi$) parameters were chosen in such a way to reproduce also the electronic transitions,[4,8] by analogy to the values reported for the similar cobalt(II) complexes.[9] The

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