$$\left.\begin{array}{r}\mathrm{Co(en)(H_2O)_3(OH)^{2+}} + \mathrm{R\cdot} \xrightarrow{k_3} \\ \text{or}\qquad\qquad \\ \mathrm{Co(en)(H_2O)_4{}^{3+}} + \mathrm{R\cdot} \xrightarrow{k_3}\end{array}\right] \rightarrow \mathrm{Co(II)} + \mathrm{R_2} + \text{other products} \qquad (3)$$

because it is small. The steady-state approximation was applied to the R· and $\mathrm{Co(en)(H_2O)_2(OH)(R)}^{n+}$ concentrations, assuming all steps after k_1 to be fast, and $-\mathrm{d}[\mathrm{Co(en)(H_2O)_4}^{3+}]/\mathrm{d}t = (2k_1K_a/[\mathrm{H}^+])[\mathrm{Co(en)(H_2O)_4}^{3+}][\mathrm{R}]$, with $k_{\mathrm{obsd}} = 2k_1K_a[\mathrm{R}]/[\mathrm{H}^+]$.

Another possibility for the disappearance of the radical would be its disproportionation. For superoxide this reaction is

$$2\mathrm{HO_2\cdot} \xrightarrow{k_4} \mathrm{H_2O_2} + \mathrm{O_2} \qquad (4)$$

and for Br·

$$\mathrm{Br\cdot} + \mathrm{Br^-} \rightarrow \mathrm{Br_2{}^-\cdot}$$

$$2\mathrm{Br_2{}^-\cdot} \xrightarrow{k_4} \mathrm{Br_3{}^-} + \mathrm{Br^-} \qquad (5)$$

This would eliminate reaction 3 if k_4 is large enough. Stoichiometrically the importance of eq 3 and 4 or 5 would not be distinguishable.

For the reaction of $\mathrm{Co(NH_3)_2(H_2O)_4}^{3+}$ with $\mathrm{H_2O_2}$, reaction 4 has been ignored in mechanistic considerations.[4] We have attempted to qualitatively measure the importance of reactions 3 and 4. R· for the $\mathrm{H_2O_2}$ reaction would be $\mathrm{HO_2\cdot}$ (the protonated superoxide ion). The pK_a of this species has been reported as 4.8[7] and k_4 has been determined to be ca. $10^6\ \mathrm{M^{-1}\ s^{-1}}$.[8] It is possible that some $\mathrm{H_2O_2}^+$ was present in our reaction solutions,[9] but this does not change the estimate of k_4.[8] $\mathrm{HO_2\cdot}$ has been reported not to reduce Co(III) complexes in several cases.[10–13] To look very qualitatively at the reaction of $\mathrm{HO_2\cdot}$ with $\mathrm{Co(en)(H_2O)_4}^{3+}$ we took a rapidly stirring solution at 25 °C that was 0.4 M in $\mathrm{HClO_4}$ and 9×10^{-3} M in $\mathrm{Co(en)(H_2O)_4}^{3+}$ and added about 7-mg amounts of solid $\mathrm{KO_2}$ to the solution four times. The visible spectrum was scanned on a Cary 14 spectrophotometer before and after the addition of all of the $\mathrm{KO_2}$ with no change in the spectrum, within experimental error, although approximately a 4 molar excess of $\mathrm{KO_2}$ had been added to the solution. Within 0.01 s after the addition of the $\mathrm{KO_2}$, the $\mathrm{HO_2\cdot}$ would be about 10^{-4} M. The steady-state concentration of $\mathrm{HO_2\cdot}$ would be less than 10^{-10} M; $[\mathrm{R\cdot}] = (k_1/k_3)(K_a/[\mathrm{H}^+])[\mathrm{R}]$ if $k_3 > k_4$. Since there is no detectable reaction at 10^{-4} M $\mathrm{HO_2\cdot}$, this would argue that $k_3 < k_4$ and probably $<10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$. Consequently, nearly all of the $\mathrm{HO_2\cdot}$ generated in solution would react with itself and not the $\mathrm{Co(en)(H_2O)_4}^{3+}$.

A similar argument can be made concerning the likelihood of Br· reacting with either $\mathrm{Co(NH_3)(H_2O)_4}^{3+}$[3] or $\mathrm{Co(en)(H_2O)_4}^{3+}$.[3] The reaction of $\mathrm{Br\cdot} + \mathrm{Br^-} \rightarrow \mathrm{Br_2{}^-\cdot}$ is very rapid, $k \approx 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$, $K \approx 10^7\ \mathrm{M^{-1}}$, and the disproportionation $2\mathrm{Br_2{}^-\cdot} \rightarrow \mathrm{Br_3{}^-} + \mathrm{Br^-}$ is also rapid, $k \approx 3.3 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.[14–16] For the reduction of Co(III) to compete, it would have to be quite rapid.

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Registry No. $\mathrm{Co(en)(H_2O)_4}^{3+}$, 67426-09-9; $\mathrm{H_2O_2}$, 7722-84-1; $\mathrm{Br^-}$, 24959-67-9.

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Synthesis and Structure of Complexes of Lanthanide Nitrates and Isonicotinic Acid Hydrazide, $\mathrm{Ln(NO_3)_3\cdot 3INH\cdot 3H_2O}$[1]

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The transition-metal complexes of isonicotinohydrazide (INH) have been a subject of occasional studies[3] for a number of years since the report[4] that INH has antitubercular properties. Recently Dutt and Sen Gupta have reported[5] the preparation of rare-earth complexes of INH of the formulas $\mathrm{Ln(ClO_4)_3\cdot 5INH}$ and $\mathrm{Ln(ClO_4)_3\cdot 3INH\cdot H_2O}$. From spectroscopic studies, they conclude that the INH bonds to the lanthanide(III) ion only by the heterocyclic nitrogen. Other lanthanide complexes of INH perchlorates[6] and chlorides[7] have been reported. There is no definitive evidence for the coordination of INH in any of these complexes.

In this paper, we report the synthesis and characterization of complexes of composition $\mathrm{Ln(NO_3)_3\cdot 3INH\cdot 3H_2O}$ and the single-crystal X-ray structure for the samarium compound. In contrast to the presumed structures previously reported, the ligand INH acts as a bidentate ligand with the heterocyclic nitrogen uncoordinated to the metal ion.

Experimental Section

The hydrated lanthanide nitrate was dissolved in a minimum amount of absolute ethanol and treated with a saturated acetonitrile–INH solution. The precipitate was filtered, washed with small portions of acetonitrile, and dried in vacuo over anhydrous calcium chloride.

Lanthanide ions were titrated with EDTA,[8] and carbon, hydrogen, and nitrogen were determined by microanalytical procedures (Midwest Microlab Ltd.); the results, summarized in Table I, are in excellent agreement with the proposed stoichiometry. The compounds are very soluble in water, methanol, and ethanol, slightly soluble in acetonitrile, and practically insoluble in nitromethane, chloroform, carbon tetrachloride, and benzene. Conductance measurements, at 25.00 ± 0.02 °C, of millimolar solutions in methanol, using a conductivity bridge composed of a Leeds and Northrup 4760 resistance box, a 2370 AC pointer galvanometer, and a cell with $K_c = 0.1070_8\ \mathrm{cm^{-1}}$, are in accordance with a 1:1 electrolyte behavior,[9] probably due to methanol's dissociative properties. The infrared spectra were recorded in a Perkin-Elmer 457 spectrophotometer in Nujol mulls between KBr plates.

The spectra lines (in $\mathrm{cm^{-1}}$) for the metal complexes are as follows: ν_{CO}, 1654–1660; $\delta_{\mathrm{NH_2}}$, 1615–1620; $\delta_{\mathrm{NH}} + \nu_{\mathrm{CN}}$, 1549–1551; ν_{CN}, 1418–1422; $\delta_{\mathrm{NH}} + \nu_{\mathrm{CN}}$, 1339–1343; CH (in plane), 1220–1222,

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Table I. Summary of Analytical Results (%) and Melting Ranges of Compounds with General Formula $Ln(NO_3)_3 \cdot 3INH \cdot 3H_2O$

	lanthanide		carbon		hydrogen		nitrogen		
Ln	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	melting ranges, °C
La	17.57	17.37	27.35	27.31	3.44	3.44	21.27	21.39	243-244
Nd	18.13	18.36	27.17	27.00	3.42	3.49	21.12	21.09	243-244
Sm	18.75	18.78	26.96	26.84	3.39	3.35	20.96	21.07	248-250
Gd	19.44	19.50	26.73	26.97	3.37	3.08	20.78	21.84	250-253
Ho	20.20	20.20	26.48	26.50	3.33	3.27	20.59	20.30	247-249
Yb	20.99	20.84	26.22	26.34	3.30	3.32	20.39	20.30	247-250

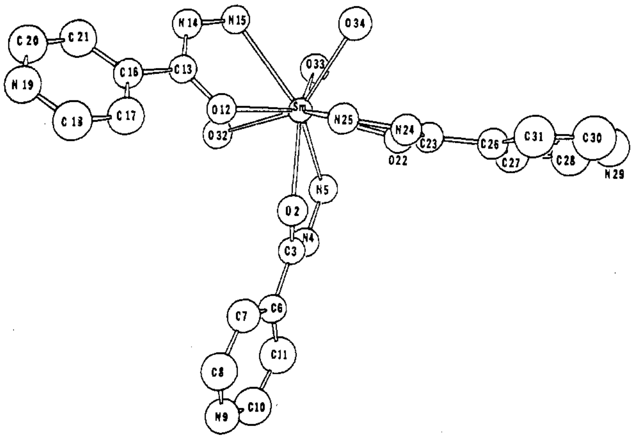

Figure 1. Atomic labeling and structure of the $Sm^{III} \cdot 3INH \cdot 3H_2O$ cation.

1075–1080, 1015–1020; CH (out of plane), 861–865. The bands attributed to the nitrate ion are as follows: ν_4, 1500–1510; ν_1, 1318–1325; ν_2, 1050–1055; ν_6, 835–840, ν_3, 768–770; ν_5, 728–732 cm^{-1}. Complete tables of conductivity values and spectral data are available in the supplementary material.

Single crystals were obtained by recrystallization of the powder obtained by the vapor-diffusion method, methanol being used as inner and acetonitrile as outer solvent. A representative single crystal of the samarium compound in an approximate parallelepiped form was ground and the resulting sphere (r = 0.15 mm) was mounted on a glass fiber and used for intensity data collection. Oscillation, Weissenberg, and precession pictures taken with Mo Kα radiation (λ 0.71069 Å) exhibit Laue symmetry $2/m$. The systematic extinctions are consistent with the monoclinic space group $P2_1/n$. Preliminary lattice constants were obtained from these photographs and refined by least squares of the diffractometer angles of 15 reflections (λ 0.71069 Å) giving the values a = 11.805 (2) Å, b = 16.050 (4) Å, c = 16.058 (3) Å, β = 100.47 (1)°, μ = 29.11 cm^{-1}, Z = 4, ρ_{calcd} = 1.660 g cm^{-3}, ρ_{obsd} = 1.70 g cm^{-3}. The conventional cell, for which the space group is $P2_1/c$ and for which correlations would be greater, has lattice constants a = 11.805 Å, b = 16.050 Å, c = 18.120 Å, and β = 119.37°.

Final intensity data were collected on a Syntex $P2_1$ autodiffractometer with Mo Kα radiation (graphite monochromator) by using the moving-crystal, moving-counter (θ–2θ) scan technique with a scan rate of 2.0°/min and a scan range from $2\theta(K\alpha_1) - 1.0°$ to $2\theta(K\alpha_2) + 1.0°$. Backgrounds were measured at each end of the scan for a total time equal to one-half of the scan time. Standard deviations were assigned[10] as $\sigma(I) = [\sigma_{counter}(I)^2 + (0.04I)^2]^{1/2}$ where $\sigma_{counter} = (I + 0.25B)^{1/2}$, I = net intensity, and B = total background counts. Of the 4251 unique data examined with $2\theta \leq 45°$, 3560 data for which $I > 2.5\sigma(I)$ were used throughout the solution and refinement process. The structure was solved by the heavy-atom method. Hydrogen atoms attached to the carbon atoms were assigned idealized positions. Hydrogen atoms attached to the nitrogen atoms were found from a difference Fourier synthesis. All hydrogen atoms were assigned thermal parameters 10% higher than the atom to which they are bonded. Isotropic least-squares refinement of nonhydrogen atomic parameters yielded $R = \sum||F_o| - |F_c|/\sum|F_o| = 0.058$, $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2} = 0.087$, and an error of fit = 3.1. The residual electron density included 2 e/Å^3 near the samarium atom and no other electron density above 1 e/Å^3. A single cycle of anisotropic refinement reduced the discrepancy factors to 0.045 and 0.067, but this did not seem justified.

Table II. Atomic Parameters for $Sm(NO_3)_3 \cdot 3INH \cdot 3H_2O$

atom	x	y	z	B, Å^2
Sm(1)	0.22553 (3)	0.22079 (3)	0.14599 (3)	1.749 (2)
O(2)	0.1454 (6)	0.3064 (4)	0.0275 (4)	2.66 (13)
C(3)	0.1839 (8)	0.3742 (6)	0.0075 (6)	2.18 (17)
N(4)	0.2892 (7)	0.4000 (5)	0.0434 (5)	2.61 (15)
N(5)	0.3593 (7)	0.3446 (5)	0.1006 (5)	2.61 (15)
C(6)	0.1125 (3)	0.4310 (6)	−0.0528 (6)	2.36 (17)
C(7)	−0.0040 (9)	0.4141 (7)	−0.0727 (7)	3.07 (21)
C(8)	−0.0750 (9)	0.4708 (7)	−0.1234 (7)	3.69 (22)
N(9)	−0.0375 (7)	0.5408 (5)	−0.1533 (6)	3.33 (17)
C(10)	0.0743 (10)	0.5536 (8)	−0.1372 (8)	4.17 (24)
C(11)	0.1542 (10)	0.5018 (8)	−0.0871 (8)	4.07 (24)
O(12)	0.0225 (6)	0.2257 (4)	0.1547 (4)	2.47 (13)
C(13)	−0.0163 (8)	0.2127 (6)	0.2221 (6)	2.16 (17)
N(14)	0.0494 (7)	0.1882 (5)	0.2924 (5)	2.55 (16)
N(15)	0.1682 (7)	0.1752 (5)	0.2915 (5)	2.43 (16)
C(16)	−0.1426 (8)	0.2248 (6)	0.2238 (8)	2.33 (18)
C(17)	−0.2178 (10)	0.2330 (7)	0.1482 (7)	3.36 (22)
C(18)	−0.3358 (10)	0.2407 (7)	0.1478 (8)	3.66 (22)
N(19)	−0.3785 (8)	0.2422 (6)	0.2182 (6)	3.24 (17)
C(20)	−0.3035 (10)	0.2362 (7)	0.2917 (8)	3.71 (23)
C(21)	−0.1868 (10)	0.2278 (7)	0.2079 (8)	3.58 (23)
O(22)	0.3273 (5)	0.1707 (4)	0.0380 (4)	2.58 (12)
C(23)	0.2874 (8)	0.1150 (6)	−0.0146 (6)	2.49 (18)
N(24)	0.1792 (7)	0.0897 (5)	−0.0248 (5)	2.55 (15)
N(25)	0.1081 (7)	0.1228 (5)	0.0304 (5)	2.53 (15)
C(26)	0.3645 (8)	0.0764 (6)	−0.0660 (6)	2.61 (18)
C(27)	0.4722 (9)	0.1083 (7)	−0.0610 (7)	3.44 (21)
C(28)	0.5504 (10)	0.0674 (8)	−0.1044 (8)	4.38 (25)
N(29)	0.5243 (8)	0.0011 (6)	−0.1508 (6)	4.04 (20)
C(30)	0.4180 (11)	−0.0275 (8)	−0.1592 (9)	5.07 (20)
C(31)	0.3342 (11)	0.0083 (8)	−0.1198 (8)	4.52 (26)
O(32)	0.1978 (6)	0.3480 (4)	0.2256 (4)	2.74 (13)
O(33)	0.4020 (6)	0.2308 (4)	0.2493 (4)	2.75 (13)
O(34)	0.2765 (6)	0.0742 (4)	0.1777 (4)	3.19 (13)
N(35)	0.0704 (7)	0.0976 (5)	0.4832 (5)	2.97 (16)
O(36)	0.0069 (6)	0.1601 (5)	0.4597 (5)	3.66 (15)
C(37)	0.0766 (7)	0.0693 (5)	0.5547 (6)	4.96 (18)
O(38)	0.1261 (7)	0.0664 (5)	0.4327 (5)	4.12 (16)
N(39)	0.4757 (7)	0.4661 (5)	0.2970 (6)	2.97 (16)
O(40)	0.5137 (7)	0.5128 (5)	0.3566 (5)	4.18 (16)
O(41)	0.3711 (6)	0.4724 (5)	0.2591 (5)	3.93 (16)
O(42)	0.5372 (8)	0.4132 (6)	0.2723 (6)	5.42 (20)
N(43)	0.3339 (8)	0.3273 (6)	0.4379 (6)	4.03 (20)
O(44)	0.2504 (10)	0.2803 (6)	0.4372 (8)	6.95 (27)
O(45)	0.4148 (9)	0.3064 (6)	0.4020 (7)	6.02 (22)
O(46)	0.3378 (9)	0.3909 (7)	0.4774 (7)	6.77 (22)

Atomic parameters, distances, and angles are given in Tables II and III. Comparisons of calculated and observed structure factors are included in the supplementary material.

Results and Discussion

The infrared studies for the complexes may be summarized as follows: (a) ν_{CO} and δ_{NH_2} shift to lower frequencies in relation to free INH,[11,12] indicating that the coordination to the lanthanide occurs through the carbonyl oxygen and amino group nitrogen; (b) ν_{CN} does not shift, indicating no strong coordination; (c) the CH out-of-plane bending mode is shifted toward higher frequencies due to a decrease in the electron density of the ring, resulting from the coordination of the ligand to the lanthanide ion;[13] (d) water bands appear at ~3600 and 1.600 cm^{-1}; (e) six bands can be attributed to nitrate ions, suggesting coordination.[14]

Table III. Significant Intermolecular Separations (Å) and Angles (deg) for $Sm(NO_3)_3 \cdot 3INH \cdot 3H_2O$[a]

		Bond Distances			
Sm–O(2)	2.397 (7)	N(9)–C(10)	1.314 (1)	C(23)–C(26)	1.487 (1)
Sm–N(5)	2.718 (5)	C(10)–C(11)	1.397 (2)	C(26)–C(27)	1.358 (1)
Sm–O(12)	2.422 (7)	C(11)–C(6)	1.392 (2)	C(27)–C(28)	1.415 (2)
Sm–N(15)	2.651 (8)	O(12)–C(13)	1.267 (1)	C(28)–N(29)	1.303 (2)
Sm–O(22)	2.420 (7)	C(13)–N(14)	1.309 (1)	N(29)–C(30)	1.320 (2)
Sm–N(25)	2.628 (8)	N(14)–N(15)	1.420 (1)	C(30)–C(31)	1.392 (2)
Sm–O(32)	2.462 (7)	C(13)–C(16)	1.508 (1)	C(31)–C(26)	1.388 (2)
Sm–O(33)	2.442 (7)	C(16)–C(17)	1.374 (2)	N(35)–O(36)	1.269 (1)
Sm–O(34)	2.458 (7)	C(17)–C(18)	1.398 (2)	N(35)–O(37)	1.224 (1)
O(2)–C(3)	1.244 (1)	C(18)–N(19)	1.319 (2)	N(35)–O(38)	1.239 (1)
C(3)–N(4)	1.338 (1)	N(19)–C(20)	1.344 (1)	N(39)–O(40)	1.234 (1)
N(4)–N(5)	1.430 (1)	C(20)–C(21)	1.370 (2)	N(39)–O(41)	1.278 (1)
C(3)–C(6)	1.477 (1)	C(21)–C(16)	1.385 (2)	N(39)–O(42)	1.229 (1)
C(6)–C(7)	1.380 (1)	O(22)–C(23)	1.251 (1)	N(43)–O(44)	1.240 (1)
C(7)–C(8)	1.395 (2)	C(23)–N(24)	1.326 (1)	N(43)–O(45)	1.239 (1)
C(8)–N(9)	1.329 (1)	N(24)–N(25)	1.430 (1)	N(43)–O(46)	1.199 (1)
		Nonbond Distances			
O(32)–O(41)	2.839 (1)	O(33)–O(45)	2.728 (1)	O(34)–O(36)	2.717 (1)
		Structural Angles			
O(2)–Sm–N(5)	62.2 (2)	N(15)–Sm–O(33)	74.9 (2)	C(18)–N(19)–C(20)	117.3 (9)
O(12)–Sm–N(15)	63.0 (2)	N(15)–Sm–O(34)	69.2 (2)	N(19)–C(20)–C(21)	124.3 (9)
O(22)–Sm–N(25)	64.0 (2)	N(25)–Sm–O(32)	139.5 (2)	C(20)–C(21)–C(16)	118.2 (9)
O(2)–Sm–O(12)	77.0 (2)	N(25)–Sm–O(33)	143.3 (2)	Sm–O(22)–C(23)	122.8 (6)
O(12)–Sm–O(22)	78.3 (2)	N(25)–Sm–O(34)	69.6 (2)	O(22)–C(23)–N(24)	122.9 (9)
O(2)–Sm–O(32)	82.3 (2)	Sm–O(2)–C(3)	126.6 (6)	C(23)–N(24)–N(25)	117.7 (8)
O(12)–Sm–O(32)	73.6 (2)	O(2)–C(3)–N(4)	121.0 (9)	N(24)–N(25)–Sm	114.6 (8)
O(22)–Sm–O(34)	72.3 (2)	C(3)–N(4)–N(5)	117.9 (8)	O(22)–C(23)–C(26)	120.8 (8)
O(2)–Sm–O(34)	138.4 (2)	N(4)–N(5)–Sm	112.3 (6)	N(24)–C(23)–C(26)	116.3 (8)
O(2)–Sm–O(33)	132.2 (2)	O(2)–C(3)–C(6)	121.2 (8)	C(26)–C(27)–C(28)	118.5 (9)
O(12)–Sm–O(33)	134.0 (2)	N(4)–C(3)–C(6)	117.8 (8)	C(27)–C(28)–N(29)	123.6 (9)
O(12)–Sm–O(34)	103.1 (2)	C(6)–C(7)–C(8)	118.4 (9)	C(28)–N(29)–C(30)	117.6 (9)
O(22)–Sm–O(32)	141.1 (2)	C(7)–C(8)–N(9)	123.9 (9)	N(29)–C(30)–C(31)	123.5 (1.3)
O(22)–Sm–O(33)	92.1 (2)	C(8)–N(9)–C(10)	116.8 (9)	C(30)–C(31)–C(26)	118.5 (1.1)
O(32)–Sm–O(33)	76.6 (2)	N(9)–C(10)–C(11)	112.7 (9)	O(36)–N(35)–O(37)	120.3 (9)
O(32)–Sm–O(34)	137.5 (2)	C(10)–C(11)–C(6)	117.6 (9)	O(36)–N(35)–O(38)	118.7 (9)
O(33)–Sm–O(34)	77.0 (2)	Sm–O(12)–C(13)	124.7 (6)	O(37)–N(35)–O(38)	121.1 (9)
N(5)–Sm–N(15)	133.7 (2)	O(12)–C(13)–N(14)	122.5 (9)	O(40)–N(39)–O(41)	120.4 (9)
N(15)–Sm–N(25)	105.7 (2)	C(13)–N(14)–N(15)	117.9 (8)	O(40)–N(39)–O(42)	121.1 (9)
N(5)–Sm–N(25)	120.4 (2)	N(14)–N(15)–Sm	110.9 (8)	O(41)–N(39)–O(42)	118.5 (9)
N(5)–Sm–O(32)	70.8 (2)	O(12)–C(13)–C(16)	120.4 (8)	O(44)–N(43)–O(45)	120.6 (1.1)
N(5)–Sm–O(32)	70.5 (2)	N(14)–C(13)–C(16)	116.1 (8)	O(44)–N(43)–O(46)	118.5 (1.1)
N(5)–Sm–O(34)	128.5 (2)	C(16)–C(17)–C(18)	119.8 (9)	O(45)–N(43)–O(46)	120.8 (1.1)
N(15)–Sm–O(32)	72.1 (2)	C(17)–C(18)–N(19)	122.2 (9)		

[a] Number in parentheses represents the estimated standard deviation of the least significant digit.

The crystallographic study of $Sm(NO_3)_3 \cdot 3INH \cdot 3H_2O$ shows a complex cation of formulation $Sm(INH)_3 \cdot (H_2O)_3{}^{3+}$. This nine-coordinate ion, pictured in Figure 1, results from the coordination of the samarium ion by three bidentate INH groups, each via the carbonyl oxygen and the amine nitrogen and by three water molecules. The nitrate ions are not involved in the inner coordination sphere of the metal ion, but one oxygen of each nitrate ion is apparently hydrogen bonded to a water molecule (O···O distances 2.72–2.84 Å).

The average Sm–O(INH) distance of 2.413 Å (range 2.397–2.422 Å) is a little shorter than the average Sm–$O(H_2O)$ distance of 2.454 Å (range 2.442–2.462 Å). The Sm–O distances must be considered a strong interaction; the Sm–O distances in the nicotinate complex[15] range from 2.36 to 2.49 Å and are considered strongly bonded. By contrast, the average Sm–N distance of 2.666 Å (range 2.628–2.718 Å) must be considered of weak strength, since the covalent radius[16] of nitrogen is only 0.04 Å greater than that of oxygen. Moreover, when corrected for the difference in radius[16] between La and Sm (0.10 Å), the extrapolated metal–oxygen distance of 2.77 Å begins to approach the 2.86-Å distance considered by Hoard and co-workers[17] to be a weak La–N interaction distance in the La(III) chelate of ethylenediaminetetraacetic acid.

The parameters in the ligands are as expected and are not noteworthy.

Two geometries have been proposed as limiting cases for nine-coordination:[18] the tricapped trigonal prism and monocapped square antiprism. We find that the coordination polyhedron for triaquotris(isonicotinic acid hydrazide)samarium(III) ion is best described as a tricapped trigonal prism, with the three water molecules forming the caps.

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Registry No. $La(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-85-4; $Nd(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-87-6; $Sm(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-89-8; $Gd(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-91-2; $Ho(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-93-4; $Yb(NO_3)_3 \cdot 3INH \cdot 3H_2O$, 70046-95-6.

Supplementary Material Available: Tabulated structure factors, a table of conductivity values, tables of spectral data, and a packing diagram (19 pages). Ordering information is given on any current masthead page.

References and Notes

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Metal Isotope Shifts in the Raman Spectrum of $Mo_2(O_2CCH_3)_4$

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Metal isotope substitution has been widely used for the assignment of metal–ligand vibrations of coordination compounds, but the application of this technique to compounds containing M–M bonds is very limited.[2] In this work we report the results of a Raman study of $Mo_2(O_2CCH_3)_4$ in the normal isotopic (ca. ^{96}Mo) and ^{92}Mo forms. $Mo_2(O_2CCH_3)_4$ has a Mo–Mo bond distance of 2.09 Å resulting from the Mo–Mo quadruple bond supported by four bridging acetate groups. Cotton and co-workers assigned the Raman feature at 404 cm^{-1} as the symmetric Mo–Mo stretch, with no significant contribution from other stretching or bending modes, whereas Ketteringham et al. concluded that the Mo–Mo stretch contains about a 15% contribution from the O_4M–MO_4 deformation.[3,4] Also, the question is open as to whether the contrast between the broad spread of Mo–Mo stretching frequencies and the narrow range of Mo–Mo bond distances reflects trends in bonding or simply the influence of coupling of the Mo–Mo stretch to Mo–ligand displacement coordinates.[5]

The purpose of this study is to (1) confirm the assignments of metal-dependent vibrations, particularly the metal–metal stretching mode, (2) infer the extent of mixing between the M–M coordinate and other internal displacement coordinates, and (3) provide data which will permit a more precise solution of the normal-coordinate vibrational problem.

Experimental Section

The natural-abundance $Mo_2(O_2CCH_3)_4$ was prepared by refluxing acetic acid containing acetaldehyde with $Mo(CO)_6$.[6] The ^{92}Mo-substituted species was prepared from $^{92}Mo(CO)_6$ by using the same procedure. The $^{92}Mo(CO)_6$ was prepared by the reaction of $^{92}MoO_3$ with carbon monoxide at 14 000 psi.[7]

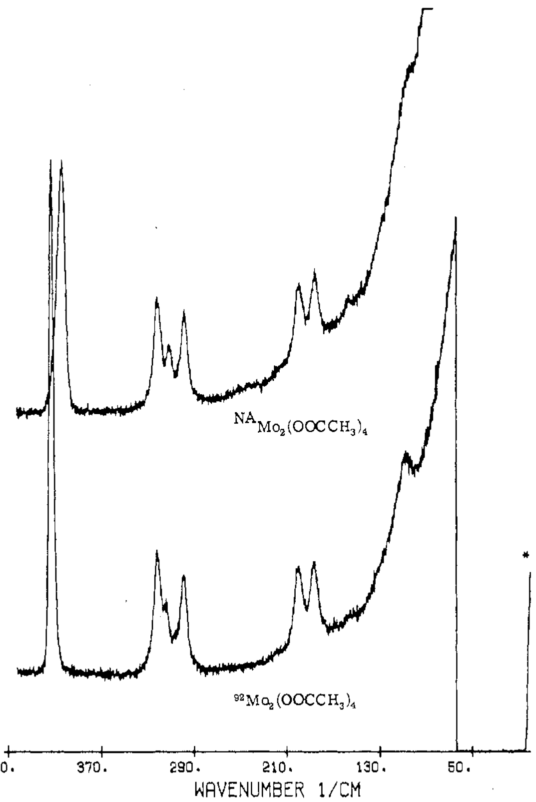

Figure 1. Room-temperature Raman spectra of $^{NA}Mo_2(O_2CCH_3)_4$ and $^{92}Mo_2(O_2CCH_3)_4$; * denotes the laser exciting line.

Table I. Raman Data for $^{NA}Mo_2(OOCCH_3)_4$ and $^{92}Mo_2(OOCCH_3)_4$[a]

$^{NA}Mo_2$-$(OOCCH_3)_4$	$^{92}Mo_2$-$(OOCCH_3)_4$	shift[b]
186	186	
200	200	
298	299	−1
311	314	−3
321	322	−1
404	413	−9

[a] Values in cm^{-1}; accuracy ±1.0 cm^{-1}. [b] Shift is for $\nu[^{NA}Mo_2(OOCCH_3)_4] - \nu[^{92}Mo_2(OOCCH_3)_4]$.

Raman spectra were collected on samples of natural-abundance (NA) and ^{92}Mo (97.4%) $Mo_2(O_2CCH_3)_4$ which were sealed under an inert atmosphere in 5-mm Pyrex tubes. Data were collected in the backscattering geometry with a Raman spectrometer which is described elsewhere.[8] The 514.5-nm Ar^+ ion laser line was employed for all spectra.

Results

The room-temperature spectra of the compounds are illustrated in Figure 1 and the data and isotope shifts summarized in Table I. The spectrum of the natural-abundance material is in good agreement with that reported by Cotton.[3] The band at 404 cm^{-1} in the natural-abundance $Mo_2(O_2CCH_3)_4$ spectrum appears at 413 cm^{-1} in $^{92}Mo_2(O_2CCH_3)_4$. Naturally abundant molybdenum contains 16% ^{92}Mo, five isotopes in the range 94 through 98, and 9% ^{100}Mo. The peak in the natural material is taken as representative of ^{96}Mo, which is in the middle of the most abundant group of isotopes.

A less intense triplet of absorptions occurring between 290–320 cm^{-1} is found 1–3 cm^{-1} higher in the compound containing the lighter molybdenum isotope. On the basis of simple consideration of reduced masses and relative force constants a larger isotopic shift is predicted for the Mo–Mo

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