

Complexes of Silver Nitrate in Solution.—Since silver nitrate is associated to a certain extent in acetonitrile,^{33,34} it was of interest to determine whether the nitrate-silver bonds of the compound $2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$ would prevail in acetonitrile. The infrared spectra of $2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$, $\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$, and silver nitrate in acetonitrile all show the same features in the regions where absorptions due to the nitrate ligand are expected. Unfortunately, the solvent absorbs strongly in these regions, *viz.*, 1410, 1270, and 1030 cm^{-1} . Intensification of absorption is perceptible at 1270 cm^{-1} , and this suggests the possibility of nitrate ion deformation,³⁴ presumably by interaction with the silver ion. In any event, the infrared spectra are consistent with the interpretation that a common type of nitrate-silver species exists in these solutions.

That the species conducting electricity in solutions of $2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$ and in solutions of $\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$ in acetonitrile are alike is indicated by the same molar conductance of these substances (Table IV). The molar conductances at the concentrations cited indicate the presence of 1:1 electrolytes.³⁵ The average molecular weight calculated for complete dissociation of $2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$ into 2Ag^+ , 2NO_3^- , and $(\text{CN})_2\text{C}_2\text{H}_4$ is 84, while dissociation to Ag^+ , $\text{Ag} \cdot (\text{CN})_2\text{C}_2\text{H}_4$, and 2NO_3^- leads to an average molecular weight of 105. The molecular weight in ethanol determined with an osmometer was 108.

The ultraviolet $n-\pi^*$ absorption of nitrates has been observed at lower wavelengths for those nitrates in which the separation of the nitrate infrared ν_1 and ν_4 frequencies is larger.³⁶ The absorption maxima in

(33) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

(34) C. B. Baddiel, M. J. Tait, and G. J. Janz, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 5S.

(35) (a) A. W. Cordes and T. V. Hughes, *Inorg. Chem.*, **3**, 1640 (1964); (b) P. Walden, *Z. Physik. Chem.*, **54**, 182 (1906); (c) P. Walden and E. J. Birr, *ibid.*, **144**, 269 (1949).

TABLE IV
ABSORPTION MAXIMA AND CONDUCTIVITY OF SILVER
COMPLEXES IN ACETONITRILE

Compd	Ultraviolet maxima, $m\mu$	Molar conductivity, $\text{cm}^2/\text{ohm-mole}$	Concn, M
$2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$	313, 314 ^a	120	0.0122
$\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$	313	123	0.0123
AgNO_3	313, 314 ^a		
LiNO_3	299, 303 ^{a,b}		
$\text{AgClO}_4 \cdot 2(\text{CN})_2\text{C}_2\text{H}_4$		155	0.0126
$\text{AgBF}_4 \cdot 2(\text{CN})_2\text{C}_2\text{H}_4$		156	0.0127

^a Maxima in tri-*n*-butyl phosphate solvent. ^b Data from J. L. Woodhead, *J. Inorg. Nucl. Chem.*, **27**, 1111 (1965).

acetonitrile for $2\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$, $\text{AgNO}_3 \cdot (\text{CN})_2\text{C}_2\text{H}_4$, and silver nitrate are at $313\text{ m}\mu$. Since the $n-\pi^*$ maximum is sensitive to the nature of the cation and to solvent effects, there is good indication that the environment about the nitrate ion is approximately the same for the three compounds, namely, that the extent of nitrate-solvent and nitrate-silver interactions are the same.

The lower wavelength of the maxima for solutions of lithium nitrate in acetonitrile and in tri-*n*-butyl phosphate is in accord with the charge to size ratio³² (e^2/r) of lithium (1.64) compared to silver (0.78). This latter consideration, however, should not detract attention from the affinity of silver(I) for nitrate ions. Association of ions in molten silver nitrate is indicated by Raman spectra.³⁷

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(36) See footnote b, Table IV.

(37) G. J. Janz and D. W. James, *J. Chem. Phys.*, **35**, 739 (1961).

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The Infrared Spectra of Rare Earth Metal Chloride Complexes of 2,2'-Bipyridyl and 1,10-Phenanthroline from 650 to 70 cm^{-1}

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The infrared spectra of rare earth metal chloride complexes of 2,2'-bipyridyl and 1,10-phenanthroline are reported from 650 to 70 cm^{-1} . From the infrared spectra in this region, frequency assignments are suggested for the ν_{M-N} vibrations. The position of the ν_{M-N} vibration is observed to vary with the properties of the metal and ligand.

Introduction

It has been generally believed that the only stable complexes of the rare earth elements involved oxygen-

containing ligands. However, recently stable complexes involving nitrogen-containing ligands have been prepared. For example, Hart and Laming² isolated stable solid 1,10-phenanthroline complexes of

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission; presented at the Fourth Pacific SAS Conference, Pasadena, Calif., Sept 22-24, 1965.

(2) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, **26**, 579 (1964).

several rare earths, and Sinha³ has prepared several 2,2'-bipyridyl complexes. The infrared spectroscopic studies of rare earth-nitrogen ligand complexes have thus far been limited to Sinha's investigation of seven rare earth 2,2'-bipyridyl complexes³ from 4000 to 650 cm^{-1} . The far-infrared spectra of these complexes have not been measured. In view of the fact that low-lying vibrations involving metal-ligand bonds would be expected to occur in the region below 400 cm^{-1} , it was decided to examine the complexes of ten rare earth, scandium, and yttrium chlorides with 2,2'-bipyridyl and 1,10-phenanthroline in the infrared region down to 70 cm^{-1} . The results obtained from this study are reported in this paper.

Experimental Section

Preparation of Complexes. 2,2'-Bipyridyl Complexes.—These complexes were prepared from the rare earth chlorides and 2,2'-bipyridyl using the method described by Sinha.³ The rare earth chlorides used in the preparation were prepared from the oxide by dissolution in concentrated HCl. The 2,2'-bipyridyl was recrystallized from petroleum ether prior to use.

1,10-Phenanthroline Complexes.—These complexes were prepared from the rare earth chlorides and 1,10-phenanthroline, using the method of Hart and Laming.² The 1,10-phenanthroline was recrystallized from petroleum ether prior to use. The complexes were washed once with warm benzene. The analytical results are tabulated in Table I. The C, H, and N results were obtained by standard microanalytical techniques. The analyses for the metals were determined by EDTA titrations and the halides by gravimetric precipitation with the silver ion. All analyses were made after drying the solid at 110° for 2 hr.

TABLE I
ANALYTICAL RESULTS OF $M^{3+}X_2Cl_3 \cdot zH_2O$ COMPLEXES

M^{3+}	z	X = bipyridyl			M^{3+}	Cl ⁻	M	z	X = 1,10 phenanthroline			M^{3+}	Cl ⁻		
		C	H	N					C	H	N				
Sa	1	Calc.	49.37	3.77	11.63	9.33	22.02	Se	4	Calc.	49.38	4.14	9.60	18.22	
		Found	50.62	3.86	10.06	9.80	19.51			Found	48.89	3.16	9.86	20.03	
Y	1	Calc.	45.70	3.45	10.66	16.91	20.23	Y	0	Calc.	51.99	2.90	10.05	16.00	19.14
		Found	46.89	3.64	10.61	16.98	20.71			Found	52.54	3.05	10.00	15.95	18.14
La	1	Calc.	41.73	3.15	9.73	24.13	16.40	La	1	Calc.	46.22	2.91	8.98	22.27	17.05
		Found	41.44	3.31	9.90	23.54	18.42			Found	46.78	2.95	9.30	21.32	16.40
Nd	1	Calc.	41.35	3.12	9.64	24.83	15.31	Nd	1	Calc.	45.82	2.82	8.91	22.93	16.91
		Found	42.40	3.34	9.53	24.85	15.56			Found	46.76	2.89	9.05	22.70	16.79
Sm	1	Calc.	40.92	3.09	9.54	25.61	15.12	Sm	1	Calc.	45.35	2.85	8.82	23.67	15.74
		Found	42.01	3.13	9.63	25.16	17.37			Found	45.95	2.82	8.74	23.34	16.72
Eu	1	Calc.	40.80	3.08	9.52	25.81	15.07	Eu	0	Calc.	45.59	2.81	9.05	24.56	17.19
		Found	41.78	3.05	9.54	25.25	17.94			Found	45.44	2.76	9.10	24.28	17.11
Gd	2	Calc.	39.25	3.29	9.15	25.69	17.38	Gd	1	Calc.	44.90	2.82	8.73	24.49	16.56
		Found	39.97	3.32	9.04	26.00	17.78			Found	44.63	2.88	9.02	24.77	17.38
Dy	1	Calc.	40.09	3.03	9.35	27.12	17.75	Dy	0	Calc.	45.21	2.56	8.90	25.82	16.90
		Found	40.78	3.02	9.33	27.92	18.27			Found	45.50	2.55	8.79	25.15	16.83
Ho	1	Calc.	39.92	3.02	9.31	27.41	17.65	Ho	0	Calc.	45.63	2.55	8.87	26.11	16.84
		Found	39.89	3.12	9.27	27.44	18.32			Found	46.54	2.95	9.12	24.70	17.25
Er	0	Calc.	40.99	2.75	9.56	28.54	15.15	Er	0	Calc.	45.46	2.54	8.84	26.38	16.78
		Found	40.83	2.97	9.36	28.51	17.97			Found	45.71	2.74	9.14	25.84	16.62
Tm	1	Calc.	39.66	3.00	9.25	27.89	17.56	Tm	0	Calc.	45.35	2.54	8.81	26.57	16.73
		Found	40.34	3.04	9.66	27.82	17.90			Found	45.62	2.82	9.75	25.42	16.34
Lu	2	Calc.	38.15	3.20	8.90	27.79	16.59	Lu	0	Calc.	44.92	2.51	8.73	27.26	15.57
		Found	37.98	2.90	8.88	26.10	21.02			Found	45.18	2.79	8.93	26.90	14.11
Gd ^a	1	Calc.	33.93	2.49	7.70	21.62	-----			Calc.	-----	-----	-----	-----	-----
		Found	33.32	2.50	7.83	21.33	-----			Found	-----	-----	-----	-----	-----

^a Bromide.

Infrared Measurements.—Spectra in the 4000–700- cm^{-1} region were obtained with a Perkin-Elmer No. 421 spectrophotometer, using Nujol mulls. For the Nujol mulls in the 4000–700 cm^{-1} region sodium chloride windows were used. No evidence for reaction with the windows was observed. The region from 700 to 300 cm^{-1} was obtained with a Beckman IR-7 equipped with a CsI prism. For the spectra below 300 cm^{-1} a Perkin-Elmer No. 301 double-beam grating spectrophotometer with a dry-nitrogen gas purge was used. Results below 700 cm^{-1}

down to 70 cm^{-1} were obtained using Nujol mulls with polyethylene windows.

Results and Discussion

The infrared frequencies from 650 to 70 cm^{-1} of 2,2'-bipyridyl and 1,10-phenanthroline complexes of ten rare earth elements, scandium, and yttrium are tabulated in Tables II and III. Some typical infrared spectra from 330 to 70 cm^{-1} are shown in Figures 1–3. Qualitative interpretation of the spectra shows that the ligands are chelated to the metal. The observed bands in the far-infrared region are tentatively assigned to vibrations involving metal-nitrogen of the ligand. These suggested assignments are tabulated in Table IV. Figure 4 presents a plot of the metal-nitrogen stretching frequency vs. the polarizing power of the metal ion.

The results obtained in the 4000–650- cm^{-1} region are in agreement with those reported by other workers for similar complexes of some rare earth metals and tran-

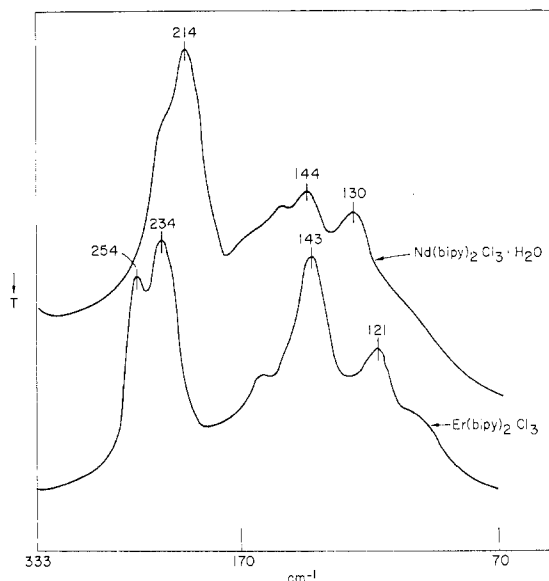


Figure 1.—Typical rare earth chloride-2,2'-bipyridyl complex spectra: $Nd(bipy)_2Cl_3 \cdot H_2O$ and $Er(bipy)_2Cl_3$.

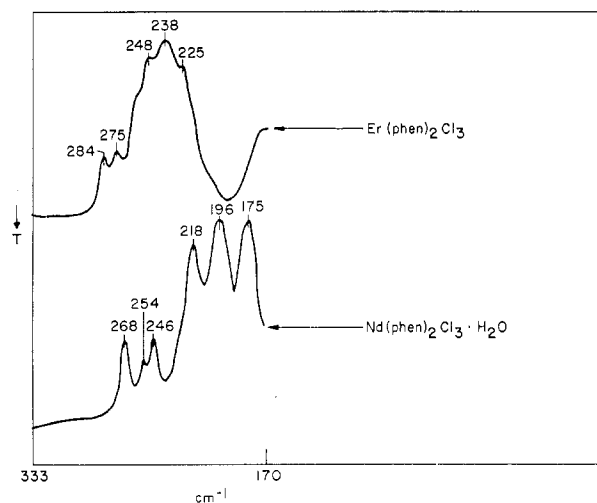


Figure 2.—Infrared spectra (333–170 cm^{-1}) of $Er(phen)_2Cl_3$ and $Nd(phen)_2Cl_3 \cdot H_2O$.

TABLE II
 INFRARED SPECTRA OF 2,2'-BIPYRIDYL COMPLEXES (650-70 cm^{-1}) (NUJOL MULLS)

2,2'-Bipyridyl	Sc	Y	La	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Lu
655 (vw)	658 (m)	657 (m) 652 (sh)	655 (sh) 649 (w)	654 (w) 644 (m)	654 (vw) 645 (w)	663 (w) 652 (sh) 645 (m)	654 (sh) 645 (w)	655 (sh) 647 (m)	654 (m) 646 (s)	654 (w) 646 (m)	654 (sh) 647 (m)	652 (m)
624 (vw-b)	638 (w)	633 (w)	630 (w)	626 (m)	626 (w)	626 (w)	627 (w)	630 (w)	629 (m)	629 (w)	629 (m)	633 (m) 612 (m) 445 (w) 428 (vw)
		436 (sh)				471 (vw-b)						436 (vw)
405 (m)	423 (m) 407 (sh)	423 (s)	419 (m)	414 (s)	417 (m)	416 (m)	415 (m)	418 (m)	416 (s)	418 (m)	419 (s)	416 (m) 404 (w) 393 (sh)
	364 (s)	357 (w-b)	355 (vw-b)	349 (w-b)	349 (w)	349 (w)	349 (w)	354 (w-b)	351 (w-b)	355 (w-b)	356 (vw-b)	338 (w)
	342 (s-b) 300 (sh)											
	287 (s)	263 (s)					249 (sh)	249 (sh)	249 (sh)	254 (s)	256 (s)	260 (s)
	245 (m)	243 (vw)	230 (sh)				233 (s)	233 (s)	231 (s)	234 (s)	235 (s)	243 (s)
	232 (vw)	230 (m)	210 (s)	214 (s)	215 (s)	217 (s)	222 (sh)		224 (sh)		224 (sh)	
	193 (w)	180 (w)				199 (sh) 171 (w)						
164 (s)		148 (w)	152 (m)	144 (w)	147 (w)	148 (w)	148 (w)	139 (m)	141 (m)	143 (s)	143 (m)	137 (m)
	134 (w)		134 (m)	130 (vw)	132 (sh)	133 (vw)	134 (vw)					
	123 (vw)	122 (vw)	118 (m)				117 (vw)	117 (vw)	121 (vw)	121 (vw)		121 (m)
92 (m)			93 (m)									

 TABLE III
 INFRARED SPECTRA OF 1,10-PHENANTHROLINE COMPLEXES (650-70 cm^{-1}) (NUJOL MULLS)

1,10-Phenanthroline ^a	Sc	Y	La	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Lu
	648 (s)	663 (m) 648 (w)	664 (m)		662 (m) 638 (vw)	663 (m) 639 (m)	663 (m) 645 (w)	662 (m) 640 (m)	663 (m) 640 (m)	643 (m)	663 (m) 641 (m)	660 (m) 640 (m)
620 (w)	628 (vw-b) 606 (vw-b) 556 (w) 504 (vs-b)	588 (w-b)	608 (m) 538 (vs)	633 (s)					556 (w)		556 (w)	
			460 (s)			515 (w) 478 (vw)	522 (w) 482 (vw)	518 (w) 480 (w)	515 (w)	518 (w)	515 (w)	468 (m-b) 420 (m)
404 (w)	426 (s) 374 (vs-b) 345 (vs-b)	426 (m)	420 (s)	420 (m)	418 (m)	420 (s)	424 (m)	422 (s)	421 (s)	422 (s)	421 (s)	390 (w-b)
	283 (s)	281 (sh)	264 (w)	268 (m)	270 (w)	274 (w)	283 (m)	279 (w)	282 (vw)	284 (vw)	284 (vw)	287 (vw)
257 (w)	275 (s)	263 (s)	252 (vw)	254 (w)	256 (vw)				274 (vw)	275 (vw)	276 (w)	278 (w)
240 (m)	240 (w) 226 (w) 212 (vw)	240 (sh)	244 (w)	246 (w)	246 (w)	235 (s)	235 (s)	247 (sh)	246 (sh)	248 (sh)	248 (sh)	248 (sh)
			218 (m)	218 (m)	216 (m)	204 (vw)	224 (sh)	238 (s)	235 (s)	238 (s)	224 (sh)	238 (s)
		191 (m)	197 (s)	196 (m)	199 (m)	198 (vw)			224 (sh)	225 (sh)	224 (sh)	224 (s)
	178 (w)	174 (w)	178 (m)	175 (m)	175 (m)	174 (w)	176 (m)	178 (m)	163 (m)	169 (w)	169 (m)	172 (m)
146 (m)		148 (w)	152 (m)	156 (sh)		155 (w)	157 (m)					
			143 (m)	148 (m-b)	148 (m-b)	143 (m)	143 (w)	143 (m)	143 (w)	143 (w)	143 (m)	144 (m)
	134 (sh)	130 (m)	134 (sh)			138 (w)						
116 (s)	118 (m)	120 (w)	125 (w)	126 (sh)	130 (sh)	123 (w)	126 (w)	130 (w)	125 (w)	130 (vw)	130 (w)	130 (sh)
		108 (sh)	104 (w)	107 (w)	112 (w)		117 (vw)		114 (vw)	116 (vw)	116 (vw)	120 (vw)
		92 (vw)					104 (vw)		99 (vw)		102 (vw)	103 (vw)

^a Starting material for formation of complexes; may be a mixture of anhydrous and hydrated material.

 TABLE IV
 SUGGESTED ASSIGNMENT FOR THE RARE EARTH-NITROGEN STRETCHING VIBRATIONS IN RARE EARTH METAL-CHLORIDE COMPLEXES OF 2,2'-BIPYRIDYL AND 1,10-PHENANTHROLINE (cm^{-1})

	Complexes	
	2,2'-Bipyridyl	1,10-Phenanthroline
La	210 (s)	178 (m), 197 (s), 218 (m)
Nd	214 (s)	175 (m), 196 (m), ^a 218 (m)
Sm	215 (s)	175 (m), 199 (m), ^a 216 (m)
Eu	217 (s)	235 (s)
Gd	222 (sh), 233 (s), 249 (sh)	224 (sh), 235 (s)
Dy	233 (s), 249 (sh)	238 (s), 247 (sh)
Ho	224 (sh), 231 (s), 249 (sh)	224 (sh), 235 (s), 246 (sh)
Er	234 (s), ^a 254 (s)	225 (sh), 238 (s), 248 (sh)
Tm	224 (sh), 235 (s), ^a 256 (s)	224 (sh), 237 (s), 248 (sh)
Lu	243 (s), ^a 260 (s)	224 (s), 238 (s), ^a 248 (sh)
Sc	287 (s)	275 (s), 283 (s)
Y	263 (s)	263 (s), 281 (sh)
(Bipyridyl)	No absorptions	(Phenanthroline)
		240 (m), 257 (w)

^a Strongest band, where two strong bands appear.

sition metals.³⁻⁶ The results tend to substantiate the interpretations made in previous publications that the

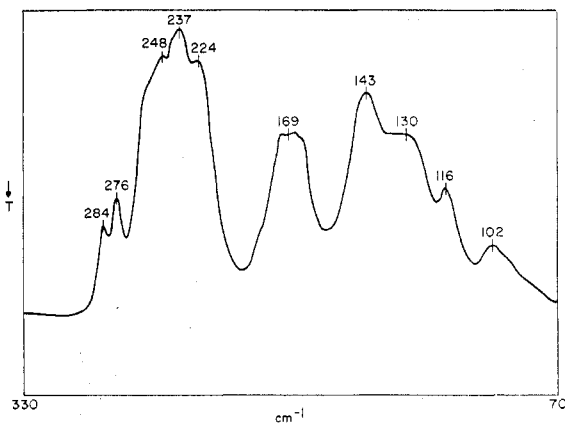


Figure 3.—Spectrum of $\text{Tm}(\text{phen})_2\text{Cl}_3$ from 330 to 70 cm^{-1} .

2,2'-bipyridyl and 1,10-phenanthroline ligands are coordinated to the metal. In the hydrated complexes

- (4) J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, **4**, 1382 (1965).
- (5) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).
- (6) R. G. Inskeep, *ibid.*, **24**, 763 (1962).

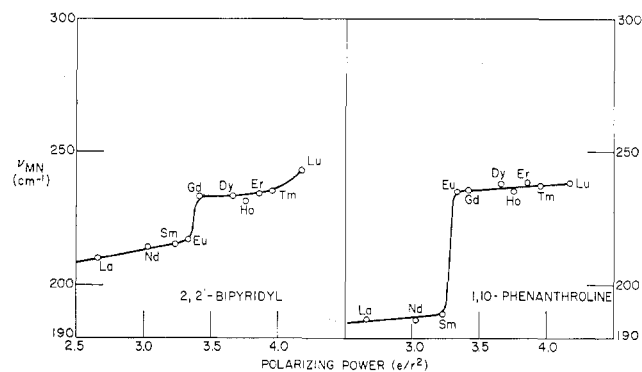


Figure 4.—Plot of ν_{M-N} vs. polarizing power of rare earth metal (e/r^2) in complexes of 2,2'-bipyridyl and 1,10-phenanthroline.

the ν_{OH} and δ_{OH} vibrations are located in the expected regions; these are absent in the anhydrous complexes.

2,2'-Bipyridyl Complexes. Infrared Spectra (650–70 Cm^{-1}).—Slight shifts are noted for the 655- and 624- cm^{-1} bands of 2,2'-bipyridyl on chelation. In addition, the 405- cm^{-1} bipyridyl band shifts to higher frequency and occasionally splits. Weak bands observed in the 350- cm^{-1} region for these chloride complexes are also observed in the bromide and iodide and are therefore not attributable to metal-halide vibrations.

Bipyridyl is free of absorptions in the region from 200 to 300 cm^{-1} , whereas the complexes show very strong absorptions (Figure 1). Table IV records these bands. The assignment of bands in this region for solid materials is very difficult because of possible coupling of modes and the appearance of multiple bands. However, certain inferences can be drawn and tentative assignments can be made. The absorption in this region does not change on dehydration and thus cannot be due to any water librational modes. The bands appear to be at too high a frequency to be assigned to lattice modes.⁷ Conversion of several compounds to the bromide and iodide fails to show significant changes in these absorptions. It would certainly be expected that, if the absorption involved metal-chloride vibrations, significant changes would be observed.⁷ In addition, if these bands were due to lattice vibrations, an anion dependency would occur. The region where these absorptions occur is not too unreasonable to attribute to rare earth metal-nitrogen stretching vibrations. Transition metal-nitrogen vibrations have been generally found at somewhat higher frequency depending on the charge of the metal⁸ and basicity of the nitrogen ligand.⁹ Other factors may be involved in determining the position of the metal-ligand band, as is the case for the ν_{M-X} vibrations in metal halides.¹⁰ Recently, copper-nitrogen stretching vibrations in 2,2'-bipyridyl complexes^{4,11} have been reported at 250–300- cm^{-1} . Since

(7) M. Goldstein, E. P. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

(8) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 150.

(9) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(10) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(11) W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965).

the mass and charge of the rare earth metals are greater than those for copper, both factors operating in opposite directions, it seems reasonable tentatively to assign the absorption in the region 200–250 cm^{-1} to the ν_{M-N} vibrations. The multiple bands observed can be caused by some solid-state effects; alternatively, if D_{2h} symmetry is postulated for the complexes, two ν_{M-N} vibrations would be expected to be infrared active; and for C_2 , four vibrations.

The position of the strongest band in the 200–250- cm^{-1} region for the rare earth complexes is plotted vs. polarizing power of the cation in Figure 4. It is observed that a gadolinium break occurs in the plot. From Gd to Tm a shallow slope is obtained, with a turnout at Lu. The over-all trend is an increase in frequency, indicative of stronger complexing, as the polarizing power increases. This lends support that this absorption involves a metal-ligand vibration. The behavior is in contrast to what would be expected for a lattice vibration. For such a vibration, the frequency would be expected to decrease as the mass increases. Since the mass increase in the rare earth series is small, the decrease in frequency should be minor. However, the results are just the opposite; and as we proceed from La to Lu, the frequency increases from 210 to 243 cm^{-1} . The abrupt change at gadolinium is not without parallel in rare earth chemistry, and the stabilization caused by a half-filled shell might be responsible for this. This behavior would tend to indicate that several factors, besides polarizing power, are operating to determine the position of the ν_{M-N} . Recent far-infrared studies with anhydrous rare earth metal nitrates showed similar trends for the M–O stretching frequency as the atomic number of M increases.¹² Yttrium and scandium are observed to show a strong absorption at higher frequencies than the rare earths, as expected, since they are d-block elements.

The infrared data between 70 and 200 cm^{-1} are more difficult to interpret since 2,2'-bipyridyl has absorptions at 164 and 92 cm^{-1} . The ten rare earth chloride-2,2'-bipyridyl complexes show several medium to weak absorptions at about 117–152 cm^{-1} . The strongest band is centered at about 140 cm^{-1} . Although some of the absorption in this region are probably associated with lattice vibrations of the ligand, bending NMN vibrations would also be expected to occur.

1,10-Phenanthroline Complexes. Infrared Spectra (650–70 Cm^{-1}).—The weak band at 620 cm^{-1} in 1,10-phenanthroline appears to be shifted toward higher frequency and intensifies upon chelation. Generally, some weak bands are found in the region of 500–590 cm^{-1} in the complexes. The 404- cm^{-1} band in the uncomplexed ligand also appears to shift to higher frequency and intensifies upon chelation.

The region between 200 and 250 cm^{-1} in the phenanthroline complexes is more complicated than in the corresponding bipyridyl complexes and therefore more

(12) A. Walker and J. R. Ferraro, *J. Chem. Phys.*, accepted for publication.

difficult to interpret. Phenanthroline itself shows weak to medium absorption at 240 and 257 cm^{-1} . Two distinct patterns of spectra are observed in this region (Figure 2). The lighter members of the series from La to Sm show a spectra with several strong to medium bands located from 175 to 220 cm^{-1} , with the strongest band at about 200 cm^{-1} . From Eu to Lu several strong bands are observed in the 235- cm^{-1} region. The shoulder at 242-248 cm^{-1} might be associated with the ligand, rather than a metal-ligand vibration. These bands are tentatively assigned to $\nu_{\text{M-N}}$ stretching vibrations, for the same reasons enumerated in the 2,2'-bipyridyl discussion. The most intense band for Sc is at 283 cm^{-1} ; for Y it is at 263 cm^{-1} . As in the bipyridyl complexes, a general trend toward higher frequency is noted with increasing atomic number. It is felt that this is related to the formation of stronger complexes. A typical spectrum, from 70 to 330 cm^{-1} , of the heavier members of the series is illustrated in Figure 3. In Table IV are tabulated the tentative assignments of the metal-nitrogen stretching vibrations in this region.

Figure 4 shows a plot of the polarizing power *vs.* the position of this most intense band in the 200-300- cm^{-1} region. A break at europium is observed. The curve is similar to the bipyridyl plot, but the rise starts at Sm rather than Eu. From Eu to Lu a rather flat line is obtained. Scandium and yttrium show absorption at higher frequency.

From Figure 4 it can be observed that the $\nu_{\text{M-N}}$ vibration in the 2,2'-bipyridyl complexes for the lower members of the rare earth series is higher than

in the 1,10-phenanthroline complexes. In the higher members this is reversed. Based on published data with transition elements the 1,10-phenanthroline complexes would have been expected to form stronger complexes and to be found at higher frequencies than the bipyridyl compounds.^{13,14}

In the region of 70-170 cm^{-1} several medium to weak bands are found. 1,10-Phenanthroline shows absorption in this region, and assignments are more difficult to make. New absorptions occur at about 170 and 140 cm^{-1} . With Sc and Y, bands are observed at about 170-212 cm^{-1} , and no absorption occurs at 140 cm^{-1} . As in the bipyridyl complexes some of the absorption in this region might be due to lattice vibrations. However, the bending NMN vibrations would also be expected in this region.

On the basis of the expected coordination number of 6 for the rare earths, it would be presumed that some of the water molecules and/or the chlorides are covalently coordinated. Some weak, broad absorptions are observed in the 300-600- cm^{-1} region and could be due to coordinated water modes.¹⁵ However, in view of the fact that no evidence for a metal chloride vibration is found from the infrared data, the metal-chloride link can be inferred to be ionic. Conductivity studies in most nonaqueous solvents are impossible because of the limited solubility of the complexes. The complexes are soluble in dimethylformamide and dimethyl sulfoxide but undergo decomposition.

(13) S. Cabani, G. Moretti, and E. Scrocco, *J. Chem. Soc.*, 88 (1962).

(14) B. R. James and R. J. P. Williams, *ibid.*, 2007 (1961).

(15) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 20, 429 (1964).

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The Coordinate Bonding in Transition Metal Complexes of 2-Carbamoyldimedone

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A number of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone complexes of the first transition metal series have been synthesized. The metal-ligand coordination has been investigated by spectral, magnetic, and proton and electron resonance measurements. The results indicate that the oxygen rather than the nitrogen of the carbamoyl group is coordinated to the metal ion. These findings are compared with the coordinate bonding reported for acetoacetamide and salicylamide complexes. Evidence of intermolecular bonding is presented, and a molecular structure is proposed.

Introduction

Since the metal-binding properties of tetracyclines, such as aureomycin and terramycin, may be related to the antibacterial action of the drugs, Albert and Rees determined the stability constants of several tetracycline-metal complexes.¹ The coordinating elements of the tetracyclines, however, have not been established.

(1) A. Albert, *Nature*, 172, 201 (1953); A. Albert and C. W. Rees, *ibid.*, 177, 433 (1956).

It is apparent that only one ring of a tetracycline is bonded to the metal, because the metal-ligand ratio is 1:2 for divalent metal ions and 1:3 for trivalent metal ions. The high acidity of the enolic proton of the diketoamide portion of a tetracycline ($\text{p}K_{\text{a}} = 3.30$ for aureomycin²) as compared to that of the other acidic protons ($\text{p}K_{\text{a}} = 7.44, 9.27$ for aureomycin²) suggests

(2) L. J. Leeson, J. E. Krueger, and R. A. Nash, *Tetrahedron Letters*, 1155 (1963).