Inorganica Chimica Acta, 18 (1976) 263–267

Alkali Earth Metal Complexes with Some Macrocyclic "Crown" Polyethers

D. G. PARSONS and J. N. WINGFIELD
Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ, U.K.
Received December 1, 1975

Alkaline earth metal perchlorates and thiocyanates react with cyclic polyethers to yield crystalline solids. The products are found to be influenced by cation radius and charge, and also by the reaction solvent and anion. Competition reactions between potassium and calcium are shown to be solvent dependent. The perchlorate and thiocyanate anions are shown by infrared spectroscopy to take part in the metal coordination in several complexes.

Introduction

The coordination chemistry of the alkali metals has been extensively studied since the initial discovery[1] of the cyclic polyethers. Complexes formed were found to depend not only on the size of the cation and polyether cavity but also on the choice of anion and solvent.[2] In this paper, we extend this study to the alkaline earth metal perchlorates and thiocyanates, and also examine some competition reactions of calcium and potassium with cyclic polyethers.

Experimental

Previously reported cyclic polyether ligands were prepared by literature methods. The preparation of substituted benzo-15-crown-5 ligands and their silver complexes will be published elsewhere. Calcium thiocyanate was used as a 50/50 w/w solution in water. The perchlorates of calcium, strontium and barium were prepared either by neutralization of the hydroxide with perchloric acid or by reaction of the chloride with silver perchlorate. Calcium tetraphenylborate was prepared by reacting calcium chloride with sodium tetraphenylborate in water and concentrating the resulting solution until crystallization occurred. Infrared spectra were taken as nujol mulls or potassium bromide discs on a Perkin–Elmer 457 Grating Spectrophotometer. Melting points were determined on a Koffler hot stage melting point apparatus. Elemental analyses were determined at the Microanalytical Laboratory, U.C.L.

Reactions in general were carried out by dissolving the reactants separately in hot solvents, followed by mixing and filtering where necessary. After crystallization or precipitation had taken place, the products were collected on a sinter, washed with a small amount of the reaction solvent, and then dried *in vacuo* at ambient temperatures.

Competition Reactions

Reactions of calcium tetraphenylborate·2(benzo-15-crown-5) with potassium iodide

A solution of potassium iodide (0.036 g) in hot methanol (10 ml) was added to a suspension of Ca $(BPh_4)_2$ 2(benzo-15-crown-5) (0.24 g) in hot methanol (10 ml), and the solution refluxed. A clear solution resulted, which was filtered hot and allowed to crystallize. Needle crystals of $KBPh_4\cdot2$(benzo-15-crown-5) were deposited (m.p. 169–71, lit.[2] 171–2° C). Yield 0.11 g, 62%.

Reaction of $Ca(NCS)_2/KNCS$ mixture with benzo-15-crown-5

(a) In ethyl acetate. A solution of benzo-15-crown-5 (0.268 g) in hot ethyl acetate (10 ml) was added to a mixture of potassium thiocyanate (0.166 g) and calcium thiocyanate/water (0.312 g) in hot ethyl acetate (20 ml), and the solution refluxed. On cooling, calcium thiocyanate·benzo-15-crown-5·H_2O separated (m.p. 279° C dec). Yield 0.09 g.

(b) In methanol. The above reaction was repeated, but on cooling, chunky crystals of KNCS·2(benzo-15-crown-5)·MeOH separated (m.p. 178–9° C). Yield 0.095 g. An authentic sample of KNCS·2(benzo-15-crown-5)·MeOH was prepared separately, having a melting point 177–9° C).

Results and Discussion

Ionic radius has been found to be an important factor in complexation of the cyclic polyethers,[1–3] and hence (see Table I) similarities may be expected between sodium and calcium, and likewise between

TABLE I. Ionic Radii.

Metal Cation	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius, Å	0.95	1.33	1.48	1.69	0.65	0.99	1.13	1.35

TABLE II. Analytical and Physical Data.

Compound	Reaction Solvent*	Analysis						M.p., °C
		Req			Found			
		C	H	N	C	H	N	
$Mg(NCS)_2 \cdot$ benzo-15-cr-5	eth. ac.	47.02	4.90	6.86	47.03	4.94	6.68	dec. >350
$Mg(NCS)_2 \cdot$ 4-nitro-benzo-15-cr-5	eth. ac.	42.36	4.19	9.26	42.20	4.29	9.03	dec. 288
$Ca(NCS)_2 \cdot$ benzo-15-cr-5	eth. ac.[a]	45.28	4.75	6.60	45.93	4.75	6.86	dec. 280
$Ca(NCS)_2 \cdot$ benzo-15-cr-5 $\cdot H_2O$	eth. ac.[b]	43.43	5.01	6.33	43.43	5.06	6.35	dec. 279–80[e]
$Ca(NCS)_2 \cdot$ benzo-15-cr-5 $\cdot$ MeOH	me	44.73	5.29	6.13	45.41	5.55	6.56	dec. 279–80[f]
$Ca(NCS)_2 \cdot$ benzo-15-cr-5 $\cdot$ py	py	50.10	5.00	8.34	50.58	5.09	8.92	dec. 280[g]
$Ca(NCS)_2 \cdot$ 4-nitro-benzo-15-cr-5 $\cdot H_2O$	eth. ac.	39.43	4.34	8.62	39.76	4.56	8.46	211–13
$Ca(NCS)_2 \cdot$ 4-methyl-benzo-15-cr-5 $\cdot H_2O$	eth. ac.	44.73	5.30	6.13	44.78	5.52	6.24	237–40[h]
$Ca(BPh_4)_2 \cdot$ 2(benzo-15-cr-5)	me[c]	75.12	6.64	–	74.68	6.62		dec. >290
$Sr(ClO_4)_2 \cdot$ 2(benzo-15-cr-5)	eth.	40.85	4.90		40.68	4.85		259–63
$Ba(NCS)_2 \cdot$ 2(benzo-15-cr-5)	ac.	45.79	5.12	3.56	45.72	5.12	3.59	167–9
$Ba(ClO_4)_2 \cdot$ 2(benzo-15-cr-5)	eth.	37.79	4.53		38.19	4.48		253–6
$Ca(NCS)_2 \cdot$ dibenzo-15-cr-5 $\cdot H_2O$	eth. ac.	48.97	4.52	5.71	48.45	4.66	5.66	292–4
$Ca(ClO_4)_2 \cdot$ benzo-18-cr-6 $\cdot H_2O$	eth.	33.76	4.57		34.11	4.42		345–7[i]
$Ca(NCS)_2 \cdot$ benzo-18-cr-6	eth. ac.	46.16	5.16	5.98	46.18	5.33	6.00	dec. >318
$Sr(ClO_4)_2 \cdot$ benzo-18-cr-6 $\cdot 3H_2O$	eth.[d]	29.43	4.63[p]		29.80	4.38		>360[j]
$Ba(ClO_4)_2 \cdot$ benzo-18-cr-6 $\cdot 2H_2O$	eth.	28.20	4.11		28.13	4.10		311–3[k]
$Ba(NCS)_2 \cdot$ benzo-18-cr-6 $\cdot H_2O$	me	37.24	4.48	4.82	36.92	4.37	4.87	dec. 277[l]
$Ca(ClO_4)_2 \cdot$ dibenzo-18-cr-6	eth.	40.09	4.01		40.67	4.17		>360
$Ca(NCS)_2 \cdot$ dibenzo-18-cr-6	eth. ac.	51.14	4.65	5.43	51.08	4.79	5.65	>360
$Sr(ClO_4)_2 \cdot$ dibenzo-18-cr-6	eth.	37.02	3.73		37.39	3.78		>360
$Ba(ClO_4)_2 \cdot$ dibenzo-18-cr-6	eth.	34.38	3.46		34.75	3.38		>360
$Ba(NCS)_2 \cdot$ dibenzo-18-cr-6 $\cdot 2H_2O$	eth.	40.66	4.31	4.31	40.92	4.17	4.42	>360[m]
$Ca(NCS)_2 \cdot$ dibenzo-24-cr-8 $\cdot H_2O$	eth. ac.	50.16	5.47	4.50	50.13	5.47	4.65	248–9[n]
$Sr(ClO_4)_2 \cdot$ dibenzo-24-cr-8 $\cdot H_2O$	eth.	38.28	4.54		38.13	4.42		226–7[o]
$Ba(ClO_4)_2 \cdot$ dibenzo-24-cr-8	eth.	36.73	4.11		36.97	4.10		265
$Ba(NCS)_2 \cdot$ dibenzo-24-cr-8	eth.	44.49	4.59	3.99	45.47	4.66	3.68	dec. 300
$Ca(BPh_4)_2 \cdot$ dibenzo-30-cr-10	ac/me	75.11	6.64		75.24	6.56		dec. >235
$Sr(ClO_4)_2 \cdot$ dibenzo-30-cr-10	eth.	40.85	4.90		40.57	4.79		250–1
$Ba(NCS)_2 \cdot$ dibenzo-30-cr-10 $\cdot H_2O$	ac.	44.59	5.24	3.47	45.19	5.20	3.45	196–7
$Ba(ClO_4)_2 \cdot$ dibenzo-30-cr-10 $\cdot 2H_2O$	eth.	37.00	4.88		37.30	4.64		216–9

* eth. ac. = ethyl acetate; me = methanol; py = pyridine; eth. = ethanol; ac. = acetone; cr = crown.

[a] $Ca(NCS)_2$ added to benzo-15-crown-5 in 1 : 1 or 1 : 2 ratio.
[b] Benzo-15-crown-5 added to $Ca(NCS)_2$.
[c] Obtained from 1 : 1 and 1 : 2 molar ratios of salt: ligand.
[d] Recrystallised from acetone.
[e] Goes opaque 160–180°.
[f] Goes opaque 170–180°.
[g] Goes opaque 170°.
[h] Loses solvent 123–6°.
[i] Loses solvent 335°.
[j] Loses solvent 220°.
[k] Loses solvent 295°.
[l] Melts at 277° if heated rapidly.
[m] Loses solvent 160°.
[n] Goes opaque 160°.
[o] Loses solvent 180°.
[p] M.wt(X-ray) 647.5; req 652.9.

4-nitro-benzo-15-cr-5 = 2-nitro-6,7,9,10,12,13,15,16octahydrobenzo-1,4,7,10,13pentaoxacyclopentadecin; 4-methyl-benzo-15-cr-5 = 2-methyl-6,7,9,10,12,13,15,16octahydrobenzo-1,4,7,10,13pentaoxacyclopentadecin.

potassium and strontium. Thus, we have undertaken a study of the coordination chemistry of the alkaline earth metals with cyclic polyethers, and the reaction conditions employed and complexes isolated are listed in Table II. As in the case of sodium,[2] calcium forms 1 : 1 and 1 : 2 complexes with benzo-15-crown-5, whereas no 1 : 1 complexes were detected for strontium and barium under any of the reaction conditions employed, which always yielded 1:2 complexes, paralleling the reactions of potassium, rubidium and caesium. The reaction of calcium thiocyanate with benzo-15-crown-5 yields 1:1 complexes, either anhydrous, or solvated with water or methanol depending on the conditions used. In addition, $Ca(NCS)_2 \cdot$benzo-15-crown-5·py is obtained when pyridine is used as solvent. $Ca(NCS)_2 \cdot 2$(benzo-15-crown-5) is not obtained under any of the conditions employed, and the reaction between calcium perchlorate and benzo-15-crown-5 is not well characterised, although the products correspond to 1:2 complexes in various stages of hydration. A well characterised 1:2 complex is however obtained when one mol of calcium tetraphenylborate is reacted with either one or two mol of benzo-15-crown-5. Thus, calcium is similar to sodium in these reactions, with the addition that (a) calcium forms a nitrogen base adduct, and (b) no 1:1 complex is isolated with calcium tetraphenylborate.

When the solubility of the benzo-15-crown-5 ligand is reduced, as in the case of 4-nitro-benzo-15-crown-5 and dibenzyloxy-benzo-15-crown-5, then the role of solvent becomes even more important. Thus, in the reaction of dibenzyloxy-benzo-15-crown-5 with calcium thiocyanate, from ethyl acetate the 1:1 complex is obtained in good yield, whereas in methanol, only the free ligand crystallizes. Similarly, the complex $Ca(NCS)_2$ ·4-nitro-benzo-15-crown-5·H_2O, obtained in good yield from ethyl acetate, dissociates when recrystallized from methanol, and yields pure ligand. In contrast, $Ca(NCS)_2 \cdot$benzo-15-crown-5·MeOH is obtained in good yield from methanol, and recrystallization of the hydrate $Ca(NCS)_2 \cdot$benzo-15-crown-5·H_2O from methanol also yields $Ca(NCS)_2 \cdot$benzo-15-crown-5·MeOH. The balance between the coordinating strength of the solvent and the lower complex stability of the less soluble substituted benzo-15-crown-5 ligands is therefore shown to be decisive in the product obtained.

The elemental analysis and nujol mull infrared spectrum of $Ca(BPh_4)_2 \cdot 2$(benzo-15-crown-5) both show the complex to be anhydrous. However, when the infrared spectrum is recorded as a potassium bromide disc, hydroxyl stretching frequencies are observed, suggesting some dissociation of the complex and subsequent complexation of K^+ with benzo-15-crown-5 (a potassium bromide disc of benzo-15-crown-5 itself shows hydroxyl stretching frequencies indicating complexation). The reaction of this 1:2 complex in methanol with potassium iodide also leads to dissociation, followed by the isolation of $KBPh_4 \cdot 2$(benzo-15-crown-5) in good yield.

$$2\,Ca(BPh_4)_2 \cdot 2(\text{benzo-15-crown-5}) + 2KI \xrightarrow{\text{MeOH}} 2[KBPh_4 \cdot 2(\text{benzo-15-crown-5}] + CaI_2 + Ca(BPh_4)_2$$

However, a similar reaction of the calcium complex with sodium tetraphenylborate in methanol yields the calcium complex unchanged. This suggests again that the reaction is governed by solubilities, since calcium tetraphenylborate is very soluble in methanol, whereas the potassium tetraphenylborate complex is rather insoluble. Likewise, sodium tetraphenylborate is much more soluble in methanol than the complex $Ca(BPh_4)_2 \cdot$ 2(benzo-15-crown-5). This conclusion is further strengthened by the direct competition reaction of potassium and calcium thiocyanates (1 mol each) with one mol of benzo-15-crown-5 in two solvents, ethyl acetate and methanol. From ethyl acetate, $Ca(NCS)_2 \cdot$ benzo-15-crown-5·H_2O is obtained, whereas from methanol, KNCS·2(benzo-15-crown-5)·MeOH is isolated.

Other complexes obtained with larger cyclic polyether rings are listed in Table III. Varying degrees of hydration are observed, but no complexes where two metals complex to one ring were isolated under a wide range of reaction conditions and reactant ratios employed. Several such complexes[4,5] have been obtained with the alkali metals and in a potassium complex,[4] the K–K distance has been found to be 3.8 Å. The

TABLE III. Hydroxyl Stretching Frequencies (cm^{-1}).

$Ca(NCS)_2 \cdot$benzo-15-crown-5·H_2O	3610(m), 3450(w,b), 3260(m), 3160(m)
$Ca(NCS)_2 \cdot$benzo-15-crown-5·MeOH	3250(s,b)
$Ca(NCS)_2 \cdot$4-nitro-benzo-15-crown-5·H_2O	3420(s,b), 3340(s,b), 3210(m), 3130(m)
$Ca(NCS)_2 \cdot$4-methyl-benzo-15-crown-5·H_2O	3420(s,b), 3200(w,b)
$Ca(NCS)_2 \cdot$dibenzo-15-crown-5·H_2O	3590(w,b), 3480(m,b), 3350(m,b), 3170(m,b)
$Ca(ClO_4)_2 \cdot$benzo-18-crown-6·H_2O	3520(s,b)
$Sr(ClO_4)_2 \cdot$benzo-18-crown-6·$3H_2O$	3540(s,b), 3480(s,b)
$Ba(ClO_4)_2 \cdot$benzo-18-crown-6·$2H_2O$	3600(m,b), 3530(s,b), 3490(sh)
$Ba(NCS)_2 \cdot$benzo-18-crown-6·H_2O	3450(m,b), 3390(m,b), 3210(w)
$Ba(NCS)_2 \cdot$dibenzo-18-crown-6·$2H_2O$	3380(m), 3340(m), 3180(w,b)
$Ca(NCS)_2 \cdot$dibenzo-24-crown-6·H_2O	3550(m), 3435(m,b)
$Sr(ClO_4)_2 \cdot$dibenzo-24-crown-8·H_2O	3620(w), 3540(s,b), 3440(m,b)
$Ba(NCS)_2 \cdot$dibenzo-30-crown-10·H_2O	3585(w,b), 3350(m,b)
$Ba(ClO_4)_2 \cdot$dibenzo-30-crown-10·$2H_2O$	3580(m,b), 3505(m,b)

increase in charge from +1 to +2 on going from the alkali metals to the alkaline earth metals is likely to make any such di-metal alkaline earth complex unstable, although a Ba–Ba distance of 4.13 Å has been observed in a barium picrate complex.[6]

Infrared Spectra

Some relevant infrared stretching frequencies of thiocyanate and perchlorate anions in the isolated complexes are listed in Tables IV and V. CN and CS stretching frequencies have together been used to determine the mode of thiocyanate bonding.[7] In the complexes studied here, ligand absorptions obscure the relevant regions except in the CN stretching frequency region, 2200–2000 cm^{-1}. The compound Ba(NCS)$_2$·2(benzo-15-crown-5) is likely to be of the sandwich type with benzo-15-crown-5 rings above and below the barium ion, the thiocyanate groups not able to coordinate, and hence giving only one stretching frequency at 2040 cm^{-1}. The compounds Ca(NCS)$_2$·benzo-15-crown-5 solvent all exhibit two CN stretching frequencies, which suggests one coordinated and one "ionic" thiocyanate. However, preliminary X-ray investigations[8] of the complex Ca(NCS)$_2$·benzo-15-crown-5·MeOH show that the calcium is coordinated on one side by the five oxygens of the benzo-15-crown-5 ring and on the opposite side by the two nitrogens of the thiocyanate groups and the oxygen of the methanol molecule. The Ca–N–C angle is different for the two thiocyanate groups (153° and 172°) and may account for the two stretching frequencies observed. No further definite conclusions may be made because the information from CS stretching and NCS bending modes are obscured by ligand absorptions.

Ca(NCS)$_2$·dibenzo-15-crown-5·H$_2$O likewise shows two CN stretching frequencies indicating inequivalent

TABLE IV. Thiocyanate Stretching Frequencies (cm^{-1}).[a]

Mg(NCS)$_2$·benzo-15-crown-5	2100(s), 2055(w)
Mg(NCS)$_2$·4-nitro-benzo-15-crown-5	2090(s), 2050(w)
Ca(NCS)$_2$·benzo-15-crown-5	2115(s), 2062(s)
Ca(NCS)$_2$·benzo-15-crown-5·H$_2$O	2100(s), 2075(s)
Ca(NCS)$_2$·benzo-15-crown-5·MeOH	2100(s), 2080(s)
Ca(NCS)$_2$·benzo-15-crown-5·pyridine	2092(s), 2075(s)
Ca(NCS)$_2$·4-nitro-benzo-15-crown-5·H$_2$O	2103(s), 2060(s,b)
Ca(NCS)$_2$·4-methyl-benzo-15-crown-5·H$_2$O	2115(s), 2072(s)
Ca(NCS)$_2$·4,5-dibenzyloxy-benzo-15-crown-5	2045(s), 1990(w)
Ca(NCS)$_2$·4,5-dimethoxy-benzo-15-crown-5	2080(b,s)
Ba(NCS)$_2$·2(benzo-15-crown-5)	2040(s), 1970(w)
Ca(NCS)$_2$·dibenzo-15-crown-5·H$_2$O	2090(sh), 2080(s), 2060(s), 2038(s)
Ca(NCS)$_2$·benzo-18-crown-6	2062(s,b)
Ba(NCS)$_2$·benzo-18-crown-6·H$_2$O	2080(s,b), 2040(sh)
Ca(NCS)$_2$·dibenzo-18-crown-6	2080(s), 2038(w)
Ba(NCS)$_2$·dibenzo-18-crown-6·2H$_2$O	2080(s), 2038(w)
Ca(NCS)$_2$·dibenzo-24-crown-8·H$_2$O	2070(s), 2035(w)
Ba(NCS)$_2$·dibenzo-24-crown-8	2060(s), 2020(w)
Ba(NCS)$_2$·dibenzo-30-crown-10·H$_2$O	2058(s), 2010(w)

[a] Weak bands at lower frequencies are thought to be isotope effects.

TABLE V. Perchlorate Asym. Bending Modes Cl–O (cm^{-1}).

Sr(ClO$_4$)$_2$·2(benzo-15-crown-5)	632(s)
Ba(ClO$_4$)$_2$·2(benzo-15-crown-5)	632(s)
Ca(ClO$_4$)$_2$·benzo-18-crown-6·H$_2$O	632(s,b)
Sr(ClO$_4$)$_2$·benzo-18-crown-6·3H$_2$O	627(s,b)
Ba(ClO$_4$)$_2$·benzo-18-crown-6·2H$_2$O	640(s), 635(sh), 628(s)
Ca(ClO$_4$)$_2$·dibenzo-18-crown-6	650(s), 642(s), 630(sh), 628(s), 624(s), 620(s)
Sr(ClO$_4$)$_2$·dibenzo-18-crown-6	646(s), 638(s), 630(s), 628(s), 625(s), 622(s)
Ba(ClO$_4$)$_2$·dibenzo-18-crown-6	640(s), 638(s), 628(s)
Sr(ClO$_4$)$_2$·dibenzo-24-crown-8·H$_2$O	646(s), 643(m), 630(s), 625(s), 622(sh)
Ba(ClO$_4$)$_2$·dibenzo-24-crown-8	632(s), 628(s), 622(s), 620(s)
Sr(ClO$_4$)$_2$·dibenzo-30-crown-10	632(s)
Ba(ClO$_4$)$_2$·dibenzo-30-crown-10·2H$_2$O	626(s)

thiocyanate groups, whereas all the other thiocyanate complexes isolated show one strong CN stretching frequency.

The perchlorate stretching and bending frequencies observed for the complexes isolated are more informative. The asymmetric Cl–O stretching frequency at ~ 1095 cm^{-1} is obscured by ligand absorptions, but the asymmetric Cl–O bending mode at ~640 cm^{-1} is observable, and the results are recorded in Table V.

The infrared spectra of $Sr(ClO_4)_2 \cdot 2$(benzo-15-crown-5) and $Ba(ClO_4)_2 \cdot 2$(benzo-15-crown-5) are identical, and both exhibit a single strong absorption at 632 cm^{-1}, suggesting ionic perchlorate groups,[9] where no coordination with the central metal has taken place. This is consistent with the proposed sandwich structure. Similarly, the strontium and barium perchlorate complexes with dibenzo-30-crown-10 show only one absorption in the 640 cm^{-1} region, suggesting again that the anions do not coordinate in these complexes. As in the similar potassium iodide complex,[10] there is the possibility of a "wrap around" complex, where no coordination of perchlorate to metal would be possible. No complex of calcium perchlorate is isolated with dibenzo-30-crown-10.

The complexes of calcium and strontium perchlorate with benzo-18-crown-6 show "ionic" perchlorate to be present. However, for the barium perchlorate–benzo-18-crown-6 complex the degeneracy is lifted, splitting the asymmetric bending frequency (640, 635 sh, 628 cm^{-1}), indicating coordination of the perchlorate groups to barium. This is borne out by preliminary X-ray results[11] which show the barium ion to be coordinated by the six oxygens of the benzo-18-crown-6 ring, one oxygen of one perchlorate group above the ring, and one oxygen of the other perchlorate group plus two water molecules below the ring giving a total coordination number of ten. The perchlorate complexes of dibenzo-18-crown-6 and dibenzo-24-crown-8 also show extensive splitting of the asymmetric bending frequency, indicating perchlorate coordination in these cases.

Acknowledgments

The authors would like to thank Dr. M. R. Truter for her support and helpful discussion during this work, and also Dr. J. D. Owen and Miss C. L. Mortimer for kindly furnishing their preliminary X-ray results.

References

1 C.J. Pedersen, *J. Am. Chem. Soc., 89,* 7017 (1967).
2 D.G. Parsons, M.R. Truter and J.N. Wingfield, *Inorg. Chim. Acta, 14,* 45 (1975).
3 C.J. Pedersen, *J. Am. Chem. Soc., 92,* 386 (1970).
4 M. Mercer and M.R. Truter, *J. Chem. Soc. Dalton,* 2469 (1973).
5 D.L. Hughes, *J. Chem. Soc. Dalton,* in the press.
6 J.A. Hamilton, L.K. Steinrauf and B. Braden, *Biochem. Biophys. Res. Commun., 64,* 151 (1975).
7 (a) J.L. Burmeister, *Coord. Chem. Rev., 1,* 205 (1966). (b) C. Pecile, *Inorg. Chem., 5,* 210 (1966).
8 J.D. Owen, personal communication.
9 (a) B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.,* 3091 (1961). (b) S.F. Pavkovic and D.W. Meek, *Inorg. Chem., 4,* 1091 (1965).
10 M.A. Bush and M.R. Truter, *J. Chem. Soc. Perkin II,* 345 (1972).
11 C.L. Mortimer, personal communication.