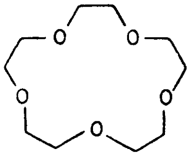
An Electron Spin Resonance Study of Crown Ethers containing Copper(II), with a d_{z^2} Ground State, and Silver Atoms

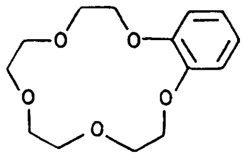
By **Julia Jezierska** and **J. Barrie Raynor,*** Department of Chemistry, University of Leicester, Leicester LE1 7RH

Electron spin resonance spectra of complexes of copper(II) chloride or copper(II) bromide with crown ethers exhibit hyper-fine coupling to two equivalent halogen atoms and have one g value very close to 2 showing that the ground state is $A_{1g}(d_{z^2})$. γ-Irradiation of the complex of silver perchlorate with crown ether in toluene or benzene yields Ag^0 centres in the crown ether.

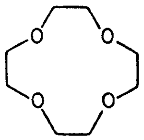
CROWN ethers form well characterised complexes with the alkali and alkaline-earth metal cations, their stability constants being very dependent upon the fit of the cation in the ligand cavity and the solvating ability of the solvent.[1] Complexes with transition-metal cations have been investigated to a lesser extent.[2,3] In this paper, we report on the e.s.r., i.r., Raman, and electronic spectra of complexes of several crown ethers with copper and silver.



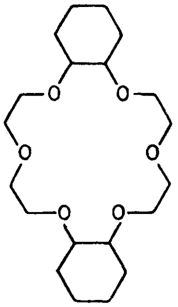
15-crown-5



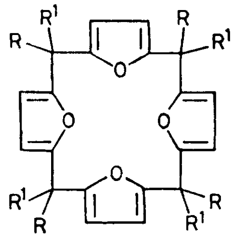
benzo-15-crown-5



12-crown-4



dicyclohexyl-18-crown-6



R = R^1 = Me
R = R^1 = Et
R = Me, R^1 = Et
R = Me, R^1 = Bu

Furan crown ethers

EXPERIMENTAL

The salts $CuCl_2$, $CuBr_2$, and $Ag[ClO_4]$ were dried by heating to 120 °C under vacuum for 24 h. Toluene, C_6H_6, $CHCl_3$, CH_2Cl_2, and CH_2Br_2 were carefully purified and dried by standard methods and kept under dry nitrogen. The crown ethers dicyclohexyl-18-crown-6, 15-crown-5, benzo-15-crown-5, and 12-crown-4 were purchased from Lancaster Syntheses and the Aldrich Chemical Company and used without further treatment. The furan crown ethers were prepared by the method of Rest *et al.*[4] All crown ethers were kept in a desiccator over P_2O_5. Electron spin resonance spectra were recorded on a Bruker ER200D spectrometer and g values calibrated against diphenylpicrylhydrazyl (dpph). Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer with a Specac low-temperature accessory and Raman spectra on a Coderg T800 spectrometer.

Approximately 10^{-4} mol dm^{-3} solutions of copper halide sin $CHCl_3$, CH_2Cl_2, or CH_2Br_2 or $Ag[ClO_4]$ in toluene or C_6H_6 were used with a three-fold excess of crown ether relative to metal. The copper halides were insoluble in the solvents used, but very slowly dissolved upon addition of the crown ether. The $CuCl_2$–crown ether solutions were orange-red and $CuBr_2$–crown ether solutions were green or yellow-green. Droplets of the $Ag[ClO_4]$ containing solutions were frozen in liquid nitrogen and irradiated for 45 min in a ^{60}Co γ-ray source. These were transferred directly to the liquid-nitrogen e.s.r. cryostat without warming up. Solutions were stored in the dark.

RESULTS AND DISCUSSION

Electron Spin Resonance Spectra.—Copper complexes. Rapidly frozen solutions of $CuCl_2$ and $CuBr_2$ with crown ethers gave well resolved spectra at 77 K showing three g features. The highest field g feature, g_z (*ca.* 2.0), of $CuCl_2$–15-crown-5 solutions exhibited hyperfine coupling to Cu (both isotopes $I = \frac{3}{2}$) and weak shoulders suggesting super hyperfine (s.h.f.) coupling to two equivalent chlorines. Second-derivative spectra showed seven well resolved lines on each copper feature with a spacing of 19 G † attributable to two equivalent chlorine atoms (^{35}Cl, 75%, $I = \frac{3}{2}$; ^{37}Cl, 25%, $I = \frac{3}{2}$). Statistically, the ^{35}Cl s.h.f.s. will dominate since coupling to two ^{35}Cl atoms will be much more probable than to two ^{37}Cl or one ^{35}Cl and one ^{37}Cl. The other g features were close together and showed no hyperfine coupling to Cu but the feature at lowest field showed weak shoulders in the second-derivative spectrum separated by 7.5 G which were attributed to Cl s.h.f.s. Figure 1 shows a typical $CuCl_2$–crown ether spectrum. The pattern of g values (*ca.* 2.00, 2.28, 2.35—2.40) (Table 1) suggests an almost axially symmetric molecule with a small splitting of the perpendicular features into their x and y components.

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† Throughout this paper: 1 G = 10^{-4} T.

Furthermore, with g_z *ca.* 2 and $g_{x,y} > 2$, the unpaired electron must be in an orbital of A_{1g} symmetry, largely comprising the d_{z^2} orbital. The spectra with benzo-15-crown-5 were similar but resolution on the highest g feature was poor with the 12-crown-4 and furan ethers, s.h.f.s. to chlorine could not be discerned with any degree of certainty.

TABLE 1

Copper spin-Hamiltonian parameters for $CuCl_2$ and $CuBr_2$ complexes with crown ethers

Halide Crown ether	$CuCl_2$ 15-crown-5	$CuCl_2$ benzo-15-crown-5	$CuCl_2$ 12-crown-4	$CuBr_2$ 15-crown-5	$CuBr_2$ benzo-15-crown-5
g_z	1.999	1.999	2.006	2.00	2.00
g_x	2.279	2.275	2.259	*ca.* 2.2	*ca.* 2.2
g_y	2.380	2.349	2.385	2.32	2.33
$g_{av.}$	2.219	2.207	2.216		
$A_z(^{63}Cu)/10^{-4}\ cm^{-1}$	121	126	126	126	126

The e.s.r. spectra of $CuBr_2$ with crown ethers at 77 K exhibited many more lines. The basic pattern of three g features and copper h.f.s. on g_z was similar to those of $CuCl_2$ with crown ethers. On the high-field g feature (z), there was a complex pattern of splitting of the copper hyperfine lines by two equivalent bromines. Careful analysis of this spectrum, aided by the second-derivative spectrum, showed that the hyperfine coupling to Br was about $\frac{3}{4}$ that of the copper. Multiple overlap of lines of varying line width due to two different copper and two different bromine isotopes added to the complexity of the spectrum, but the lines at highest field could unambiguously be used to define the bromine hyperfine coupling. The g feature at low field also showed well resolved s.h.f.s. to two equivalent bromines (^{79}Br, 50.6%, $I = \frac{3}{2}$; ^{81}Br, 49.4%, $I = \frac{3}{2}$). S.h.f.s. on the middle g feature was complicated by overlap with lines from the other two g features. Figure 2 shows the spectrum of $CuBr_2$ with 15-crown-5 in $CHCl_3$. Only poorly resolved spectra were obtained with the 12-crown-4 ether, but they had the same format as those with 15-crown-5 ethers. Solutions of copper halides with 18-crown-6 ethers yielded only a spectrum identical to that in the absence of crown ether and suggested that no adduct or interaction occurred.

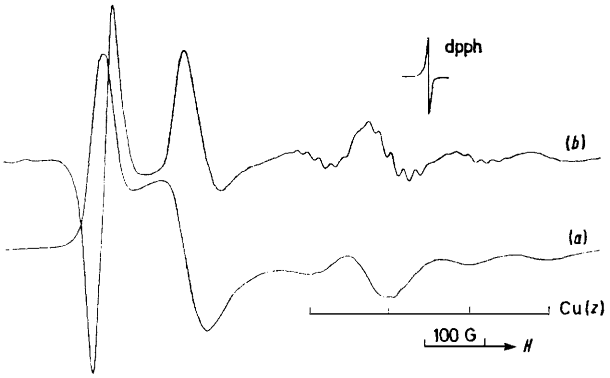

FIGURE 1 E.s.r. spectrum of $CuCl_2$ with 15-crown-5 in CH_2Cl_2 at 77 K: (*a*) first derivative and (*b*) second derivative

The spectra of $CuCl_2$ and $CuBr_2$ with crown ethers were independent of the halogen-containing solvent. This showed that the Cu–Cl or Cu–Br bonds were not breaking and exchanging with Cl or Br from the solvent. When other organic solvents were used, *e.g.* alcohols, acetone, acetonitrile, dimethyl sulphoxide, or dimethyl-

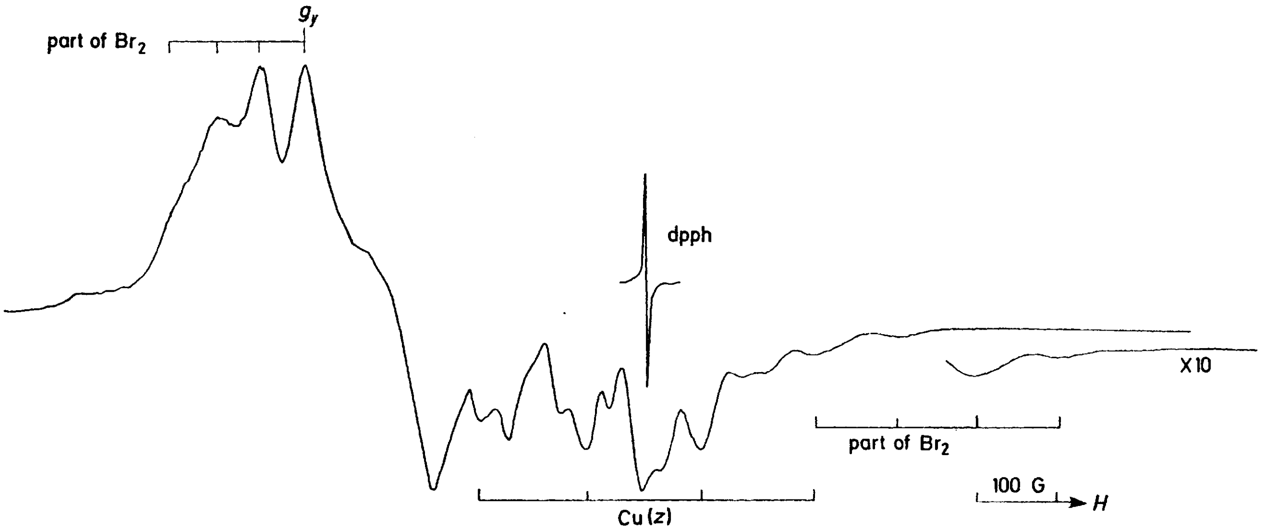

FIGURE 2 E.s.r. spectrum of $CuBr_2$ with 15-crown-5 in $CHCl_3$ at 77 K, first derivative. On g_y, the unambiguous low-field lines due to Br_2 are indicated. Likewise on g_z, the unambiguous high-field lines due to Br_2 on the copper $M_I = -\frac{3}{2}$ lines are indicated

formamide, $CuCl_2$ or $CuBr_2$ with crown ether exhibited an e.s.r. spectrum at 77 K with $g_{\parallel} > g_{\perp} > 2$ which is typical of copper complexes with the unpaired electron in a $d_{x^2-y^2}$ ground state. We believe that in these solvents the copper ion is strongly solvated and that no complex is formed with crown ethers. On some of the frozen-solution spectra of $CuCl_2$ and $CuBr_2$ with crown ethers, there was evidence of a second species which could readily be identified as the ' normal $d_{x^2-y^2}$ ' spectrum. We attribute this to solvation of some copper ions by traces of water, since addition of a drop of water to the solutions increased the proportion of this spectrum.

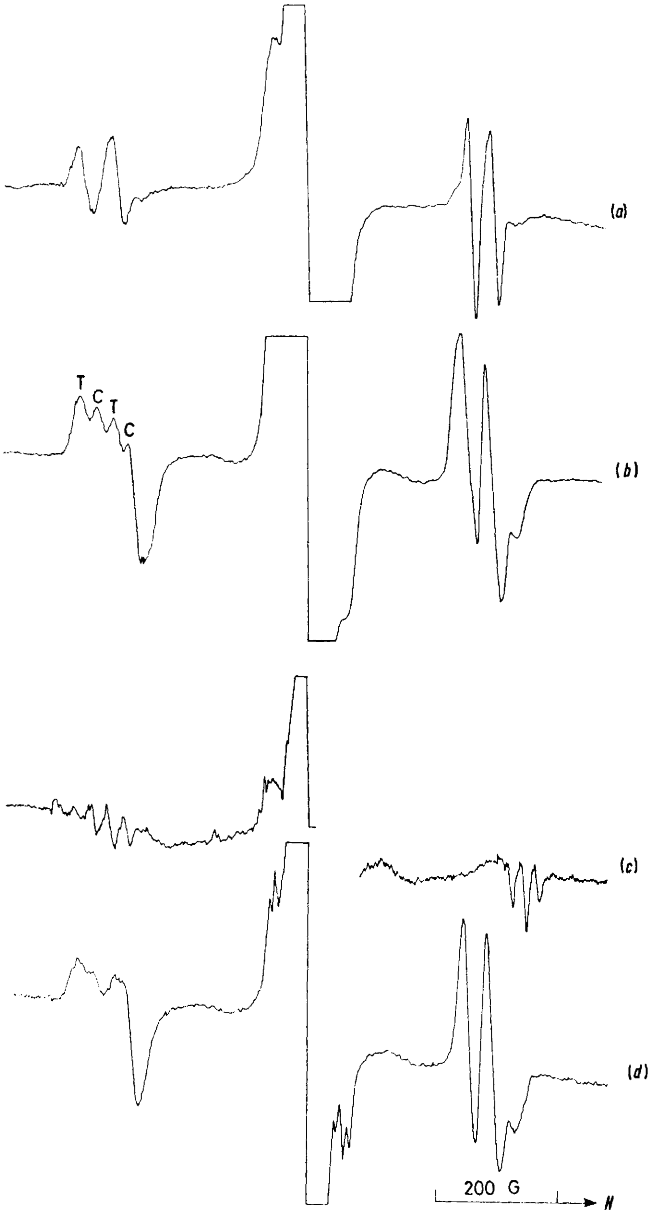

FIGURE 3 E.s.r. spectrum at 77 K of γ-irradiated $Ag[ClO_4]$ in (*a*) toluene, (*b*) toluene + dicyclohexyl-18-crown-6, (*c*) benzene, (*d*) benzene + dicyclohexyl-18-crown-6. Hyperfine structure on the central feature is due to $C_6H_6^+$

Copper complex in fluid solution. The e.s.r. spectra from all the solutions consisted of a very broad and ill defined line. Upon lowering the temperature to just above the freezing point of the solvent, the spectrum sharpened and showed four lines separated by *ca.* 65 G.

Silver centres. The spectra from γ-irradiated frozen toluene solutions containing $Ag[ClO_4]$ and dicyclohexyl-18-crown-6 showed, besides the strong signal at $g = 2$ from solvent radicals, a group of four overlapping lines at lower field, and a group of three overlapping lines at higher field. By comparison with the spectrum of a solution of irradiated toluene containing $Ag[ClO_4]$ only, which comprised two doublets only from ^{107}Ag and ^{109}Ag (each $I = \frac{1}{2}$ and similar abundance), the spectrum of the crown ether solution consists of two different Ag^0 centres. One is identical with that in toluene alone [lines marked T in Figure 3(*b*)] and is the Ag^0–toluene centre, and the other with smaller hyperfine coupling [C in Figure 3(*b*)] is attributed to a Ag^0–crown ether centre with a slightly lower g value. The relative abundance of the signals from the two radicals was very dependent upon the amount of crown ether present. The hyperfine couplings, corrected by the use of the Breit–Rabi equation, are given in Table 2. There was no e.s.r. evidence in either solution of Ag_3^+, Ag_4^+, or Ag^{2+} species.

TABLE 2

g Values and hyperfine parameters (corrected by the use of Breit–Rabi equation) for silver centres in toluene and in dicyclohexyl-18-crown-6 in toluene or benzene

	Ag^0 in toluene *	Ag^0(dicyclohexyl-18-crown-6) in toluene or benzene
$A(^{109}Ag)/G$	665 (664)	638
$A(^{107}Ag)/G$	574 (577)	557
g	1.994	1.993

* Values in brackets are those of ref. 10 for toluene.

The spectra of corresponding γ-irradiated frozen benzene solutions containing $Ag[ClO_4]$ and dicyclohexyl-18-crown-6 were very similar to those in toluene but the features at low field were slightly less well resolved. The spectrum of benzene solution containing $Ag[ClO_4]$ only was different from $Ag[ClO_4]$ in toluene and identical to that found by Forbes and Symons [5] in which Ag_2^+ ions were the dominant species. Besides the silver centres, there was present at g *ca.* 2 the well resolved spectrum of $C_6H_6^+$. In the presence of crown ether, no Ag_2^+ ions were detected, only lines analogous to those found in toluene, *viz.* arising from Ag–benzene centres and Ag^0–crown ether centres. Unsubstituted 18-crown-6 with $Ag[ClO_4]$ in benzene and in toluene behaved similarly and gave similar e.s.r. parameters. Electron spin resonance spectra were not as well resolved because of poorer solubility in the solvents used.

Analysis of halide hyperfine tensors. The large hyperfine coupling to two equivalent chlorine or bromine atoms in the Cu^{2+}–crown ether complexes gives further support to a d_{z^2} ground state for the electron on the copper atom. The value of $A_{\parallel}$ must be positive because real spin density has passed to the halogen atoms *via* the σ bond and taking $A_\perp$ as positive also, then the anisotropic hyperfine tensors may readily be deduced after deduction of the dipolar coupling term $g_N\beta_N(3\cos^2\theta - 1)r^{-3}$,[6] (where r was taken as 2.3 and 2.4 Å from typical Cu–Cl and Cu–Br bond distances respectively). From the corrected values of $A_{\text{aniso.}}$ and $A_{\text{iso.}}$, the p and s characters, respectively, of the electron on the halogen may be calculated using the values for an electron entirely in a p or s orbital.[7] The p and s characters so deduced for chlorine and bromine compare well with those for other metal halide complexes with a d_{z^2} ground state [8] and are listed in Table 3. Our results show that the delocalisation to the bromine in the $CuBr_2$–crown ether complexes is almost the same as to the chlorine in the $CuCl_2$–crown ether complexes, amounting to a total of 14—15%. Had the value of $A_\perp$ been taken as negative, an improbably high $p : s$ ratio and p character would have been obtained.

TABLE 3

Halogen hyperfine couplings and spin densities

System	$A_\parallel$/G	$A_\perp$/G	$A_{\text{iso.}}$ [a]/ G	$A_{\text{aniso.}}$ [b]/ G	s [c] character/ %	p [d] character/ %
$CuCl_2$–15-crown-5	19	7.5	11.3	7.3	0.55	7.1
$CuCl_2$–benzo-15-crown-5	19					
$CuBr_2$–15-crown-5	101	55	70	30	0.61	6.3
$CuBr_2$–benzo-15-crown-5	101	50	67	33	0.58	6.9

[a] From $A_{\text{iso.}} = (A_\parallel + 2A_\perp)/3$. [b] After subtraction of dipolar correction (0.4 G for Cl and 1.0 G for Br). [c] Using 2 044 G and 11 454 G for A_s 100% for Cl and Br respectively(ref. 7). [d] Using 102 G and 477 G for A_p 100% for ^{35}Cl and Br respectively (ref. 6).

Analysis of the copper hyperfine and g *tensors*. Full analysis of the Cu hyperfine and g tensors can only be done with limited accuracy because of the uncertain values for A_x and A_y. We have made use of the equations given by Evans *et al.*[9] for a d^1 configuration with an A_{1g} ground state of the form $\psi = ad_{z^2} + bd_{x^2-y^2}$. We have calculated a^2, b^2, P, and K for all combinations of copper hyperfine coupling both positive and negative to A_x and A_y ranging from 20 to 40 G. In all cases a^2 is found to be very close to unity showing that the unpaired electron is in an essentially d_{z^2} orbital. The value of P ranges from 310 to 340 × 10^{-4} cm^{-1} and K from 0.11 to 0.16 for hyperfine couplings ranging over 20—40 G. Since the value of P for an electron entirely in a d orbital on a Cu^{2+} ion is *ca.* 390 × 10^{-4} cm^{-1},[6] then calculated values of P for hyperfine couplings ranging from 20 to 40 G represent a range of 79 to 87% unpaired electron on the copper. Also, since the total spin density on the halogen atoms is 14—15%, and since about one third of the electron in a d_{z^2} orbital is in the equatorial 'ring', a hyperfine coupling of *ca.* 20 G, corresponding to P = 310 × 10^{-4} cm^{-1} and K = 0.11, is the most probable and is certainly consistent with the observed spectrum.

Electronic, Infrared and Raman Spectra of the Copper Complexes.—Complexes of $CuCl_2$ and $CuBr_2$ with the crown ethers in dichloromethane were intense red and green respectively. The optical spectra exhibited an absorption at 21 200 cm^{-1} for the $CuCl_2$ complex and at 15 400, 23 300, and 26 700 cm^{-1} for the $CuBr_2$ complex. The high intensity and energy of these bands suggest that they are charge transfer in origin. They may be compared with 26 000 cm^{-1} for $CuCl_4^{2-}$ and 17 000, 19 500, and 30 000 cm^{-1} for $CuBr_4^{2-}$.

The i.r. and Raman spectra were particularly informative. Spectra were recorded on frozen CH_2Br_2 solutions close to 77 K. Below 500 cm^{-1}, the i.r. spectrum showed a single absorption at 335 and 262 cm^{-1} for $CuCl_2$ and $CuBr_2$ complexes respectively. Likewise, the Raman spectrum showed absorptions at 285 and 210 cm^{-1} for $CuCl_2$ and $CuBr_2$ complexes respectively, in addition to a strong solvent absorption at 184 cm^{-1}. These absorptions are consistent with a linear $CuCl_2$ or $CuBr_2$ fragment and may be assigned to the ν_1 (Σ_g^+) symmetrical stretch (Raman active) and $\nu_3(\Sigma_u^+)$ asymmetrical stretch (i.r. active) modes in $D_{\infty h}$ symmetry. These results support the formulation of a *trans* dihalide crown ether complex suggested by the e.s.r. evidence.

Silver Centres.—Observation of Ag^0 centres in toluene have been reported by Zhitnikov *et al.*[10] and our hyperfine couplings were almost identical. Forbes and Symons [5] had detected Ag_3^{2+} ions in toluene and Ag_2^+ and Ag_4^{3+} in benzene containing traces of water. Our solvents had been carefully dried and it appears that the presence of water is crucial to the aggregating of the silver cations. We found no evidence of dimers, trimers, or tetramers in our irradiated frozen solutions. Their presence would be obvious and unmistakable. Likewise, no evidence of Ag^{2+} was seen. A perpendicular feature if present would be seen on the edge of the clear $C_6H_6^+$ central feature in benzene solutions.

An unusual feature of the benzene solution of Ag–crown ether was the disappearance of the Ag_2^+ signal in the presence of crown ether and its replacement by a spectrum of Ag^0 with parameters identical (within experimental error) to that of Ag^0 in toluene. This centre has been reported by Zhitnikov *et al.*[10] but they did not resolve the two isotopes of silver. It is not surprising that the parameters are the same since the structure of the centre in benzene and in toluene would be expected to be η^6 bonded. Salts of the formula $[Ag(C_6H_6)][ClO_4]$ are known [11] and have η^6-C_6H_6 bonded benzene and are particularly sensitive to water. It is thus not surprising that these centres are unlikely to be formed to any extent in wet solvents.

The magnitude of the $^{109}Ag^0$ h.f.s. in C_6H_6 and C_6H_5Me, 665 G, compares well with that for Ag^0 in water (702 G).[12] Comparison of our values of Ag^0 in benzene or toluene with that for Ag^0 in the gas phase (706 G) [13] shows that only *ca.* 6% of the electron is delocalised. When Ag^0 is in the crown ether, the hyperfine coupling to ^{109}Ag is less (638 G) and represents more delocalisation (9.6%) because of the efficient overlap of the 6*s* electron with orbitals of the same symmetry (A_{1g}) on the benzene.

Crown Ethers as Ion and Radical Traps.—It is well known that crown ethers will complex with many cations and molecules. Where complexes have been isolated and crystal structures determined, the cations reside in the central cavity of the crown ether. In other cases, strong evidence points to similar structures. The main factor which determines which cations will combine with which crown ethers is size. The hole diameter in 12-crown-4 is 1.2—1.5 Å, that in 15-crown-5 is 1.7—2.2 Å, and that in 18-crown-6 is 2.6—3.2 Å. Thus Cu^{2+} (diameter 1.44 Å) would be expected to complex with 15-crown-5 and 12-crown-4 but not 18-crown-6. The Ag^+ ion (diameter 2.52 Å) would be expected to complex with 16-crown-6 and the free silver atom (diameter 2.88 Å) would likewise be stabilised by the same crown ether.

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REFERENCES

[1] C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16; A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, 1968, **7**, 176; R. Humphry-Baker, M. Grätzel, P. Tundo, and E. Pelizzetti, *Angew. Chem. Internat. Edn.*, 1979, **18**, 630.

[2] J. C. G. Bunzli, D. Wessner, and H. T. T. Oanh, *Inorg. Chim. Acta*, 1979, **32**, L33; C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[3] K. Ishizu, T. Haruta, K. Nakai, K. Miyoshi, and Y. Suziura, *Chem. Letters*, 1978, 579.

[4] A. J. Rest, S. A. Smith, and I. D. Tyler, *Inorg. Chim. Acta*, 1976, **16**, 21.

[5] C. E. Forbes and M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 467.

[6] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[7] J. R. Morton and K. W. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

[8] R. P. A. Muniz, N. V. Vugman, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 1289; R. S. Eachus and R. E. Groves, *ibid.*, 1974, **61**, 2860; J. R. Shock and M. T. Rogers, *ibid.*, 1975, **62**, 2640; S. C. Jain, K. V. Reddy, and T. R. Reddy, *ibid.*, 1975, **62**, 4366.

[9] A. G. Evans, J. C. Evans, D. J. C. Espley, P. H. Morgan, and J. Mortimer, *J.C.S. Dalton*, 1978, 57.

[10] R. A. Zhitnikov, N. I. Mel'nikov, and A. L. Orbeli, *Zhur. strukt. Khim.*, 1968, **9**, 616.

[11] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1949, **71**, 3644; H. G. Smith and R. E. Rundle, *ibid.*, 1958, **80**, 5075.

[12] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc. (A)*, 1970, 1329.

[13] N. F. Ramsey, ' Molecular Beams,' Clarendon Press, Oxford, 1955.