

Second-sphere Co-ordination of Neutral and Cationic Transition Metal Complexes by Crown Ethers

By HOWARD M. COLQUHOUN

(Corporate Laboratory, Imperial Chemical Industries Ltd., P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE)

and J. FRASER STODDART

(Department of Chemistry, The University, Sheffield S3 7HF)

Summary The [ammine(η^5 -cyclopentadienyl)dicarbonyl-iron(II)] cation and the neutral complex, amminepenta-carbonyltungsten(0), form 1:1 adducts in solution with 18-crown-6 and dibenzo-18-crown-6 by virtue of hydrogen bonding between the ammine ligand in the transition metal complex and oxygen atoms of the crown ether; a crystalline adduct, $[\text{W}(\text{CO})_5\text{NH}_3 \cdot \text{dibenzo-18-crown-6}]$, has been isolated as a benzene solvate.

SINCE the concept of co-ordination of transition metal complexes in the second sphere was introduced by Werner¹ in 1913, i.r. spectroscopic evidence in the solid state and in solution has emerged for hydrogen bonding (N-H...X) between ammine ligands (NH₃ and RNH₂) in both neutral platinum² and cationic ruthenium³ complexes and electron donor atoms (X) present in other ligands, counterions, or solvents. The observed c.d. of $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{ClO}_4]_3^-$ in an aqueous solution of diethyl L-tartrate has also been interpreted⁴ in terms of some mutual orientation as a consequence of hydrogen bonding between the two species. In view of the well known⁵ ability of 18-crown-6 and its derivatives to form strong adducts with NH₄⁺ and RNH₃⁺ ions by multiple hydrogen bond formation, it seemed possible that transition metal amines would complex *via* ligating ammonia ($\text{M} \leftarrow \text{NH}_3^{\delta+}$) with crown ethers in a similar manner. Here, we present spectroscopic and analytical evidence for the formation of discrete hydrogen-bonded 1:1 adducts between crown ethers and both cationic and neutral transition metal ammine complexes.

The i.r. spectrum of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NH}_3)]^+[\text{BPh}_4]^-$ (ref. 6) in CH₂Cl₂ solution exhibits two strong CO stretching bands, a symmetric vibration (2065 cm⁻¹) and an anti-symmetric mode (2018 cm⁻¹). Addition of 1 mol. equiv. of dibenzo-18-crown-6 (DB18C6) results in a shift of these

bands to 2057 and 2010 cm⁻¹, respectively. Addition of more than 1 mol. equiv. of DB18C6 produces no further change in the carbonyl region of the spectrum. This shift to lower frequency is consistent with donation of electrons from the oxygen atoms of DB18C6 to the complex ion, where the extent of electron transfer from metal d-orbitals to CO π -antibonding orbitals is correspondingly increased, resulting in weaker CO bonds and hence lower stretching frequencies. By contrast, for the analogous pyridine complex,⁷ $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}_5\text{H}_5\text{N})]^+[\text{PF}_6]^-$ in CH₂Cl₂ solution, no shift in frequency of the CO stretching band occurs when DB18C6 is added. Our conclusion that hydrogen bonding between DB18C6 and the NH₃ ligand in $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NH}_3)]^+$ is responsible for the formation of a 1:1 adduct, and hence for the observed frequency shift, was confirmed by ¹H n.m.r. spectroscopic studies in CD₂Cl₂. On addition of 1 mol. equiv. of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NH}_3)]^+[\text{BPh}_4]^-$ to DB18C6, the AA'BB' system for the -OCH₂-CH₂O- protons, originally centred on δ 3.95 and 4.13 in the spectrum of the free crown, appears at δ 3.85 and 4.12 along with additional resonances at δ 2.15 br. (s, NH₃) and 4.52 (s, C₅H₅). These chemical shifts are to be compared with the δ values of 1.52 br. (s, NH₃) and 4.72 (s, C₅H₅) in the spectrum of the pure ammine. The 1:1 adduct $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NH}_3) \cdot \text{DB18C6}]^+[\text{BPh}_4]^-$ affords the partial spectral data: δ 1.90 br. (s, NH₃), 3.55 (s, OCH₂), and 4.96 (s, C₅H₅), *cf.* δ 3.58 (s, OCH₂ in free 18C6). Two comments can be made with reference to the spectral data for the pure ammine: (i) the shift of the NH₃ signal to lower field on addition of either crown indicates that the NH₃ ligand becomes involved in hydrogen bonding, and (ii) the shift to higher field of the C₅H₅ signal in the 1:1 adduct with DB18C6 (which is to be contrasted with the shift to lower field of the same resonance in the 1:1 adduct with 18C6)

can be explained by shielding of the C_5H_5 protons by the aromatic rings of DB18C6. On cooling the CD_2Cl_2 solution of the $[Fe(\eta^5-C_5H_5)(CO)_2(NH_3).DB18C6]^+[BPh_4]^-$ adduct, the signal at δ 3.95 for the $-CH_2OCH_2-$ protons⁸ divides ($T_c - 50$ °C) into two signals ($\Delta\nu$ 50 Hz) at -90 °C. The derived ΔG^\ddagger value of 10.8 kcal mol⁻¹ (45.2 kJ mol⁻¹) can be associated with a process involving equilibration of the cation between the homotopic faces of DB18C6 and is indicative of strong adduct formation. This finding encouraged us to examine the extent to which the neutral ammine $[W(CO)_5(NH_3)]^0$ associates with DB18C6. Indeed, a crystalline adduct which analyses for $[W(CO)_5(NH_3).DB18C6.0.5C_6H_6]$ may be isolated from benzene solution and the i.r. (C_6H_6) and 1H -decoupled ^{13}C n.m.r. (C_6D_6) spectra of this 1:1 adduct show significant differences relative to the spectra of the two components.†

Thus, crown ethers enter into second-sphere co-ordination with transition metal amines in solution and can form

crystalline adducts. Further investigations of our own,¹⁰ together with the published¹¹ X-ray crystallographic data on polymeric structures in which 18-crown-6 is hydrogen bonded to aqua ligands co-ordinated to Co^{II} , Mn^{II} , and U^{VI} , suggest the potential existence of a large family of discrete adducts in which transition metal complexes are bound to crown ether ligands by formation of hydrogen bonds.

We thank Dr. W. Hewertson (I.C.I. Corporate Laboratory) for his interest in and support of these investigations and one of us (J. F. S.) acknowledges financial support from the S.R.C. under their Cooperative Research Grants Scheme. We are grateful to Mr. I. Brown (I.C.I. Corporate Laboratory) and Drs. B. E. Mann and C. M. Spencer (Sheffield University) for determining ^{13}C n.m.r. spectra.

(Received, 17th March 1981; Com. 301.)

† $\nu(CO)$ 2067 ($A_1^{(2)}$), 1923 (E), and 1900 ($A_1^{(1)}$) cm^{-1} ; cf. i.r. data for $[W(CO)_5NH_3]$: $\nu(CO)$ 2057, 1912, and 1880 cm^{-1} ; δ (Me_4Si) 198.73 (CO_{cis}), 200.89 (CO_{trans}), 67.21, 69.79 (OCH_2CH_2O) p.p.m.; cf. ^{13}C n.m.r. data for $[W(CO)_5NH_3]$ 198.66, 200.59, and for DB18C6 69.29, 70.17 p.p.m.

¹ A. Werner, 'Neuere Anschauungen auf dem Gebiete der anorganischen Chemie,' 3rd. edn., Vieweg und Sohn, Braunschweig, 1913; see also, J. Bjerrum, *Adv. Chem. Ser.*, 1967, **62**, 178.

² J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 1956, 2712.

³ J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Chem. Soc. A*, 1971, 3168.

⁴ S. F. Mason and B. J. Norman, *Chem. Commun.*, 1965, 335; see also, W. A. Freeman, *Inorg. Chem.*, 1976, **15**, 2235.

⁵ C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1978, **11**, 8; J. F. Stoddart, *Chem. Soc. Rev.*, 1979, **8**, 85.

⁶ E. O. Fischer and E. Moser, *Inorg. Synth.*, 1970, **12**, 35.

⁷ B. D. Dombek and R. Angelici, *Inorg. Chim. Acta*, 1973, **7**, 345.

⁸ D. Live and S. I. Chan, *J. Am. Chem. Soc.*, 1976, **98**, 3769.

⁹ M. Wrighton, *Inorg. Chem.*, 1974, **13**, 905.

¹⁰ H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, unpublished results.

¹¹ T. B. Vance, E. M. Holt, C. C. Pierpont, and S. L. Holt, *Acta Crystallogr., Sect. B*, 1980, **36**, 150; T. B. Vance, E. M. Holt, D. L. Varie, and S. L. Holt, *ibid.*, p. 153; A. Knöchel, J. Kopf, J. Oehler, and G. Rudolph, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 61; G. Bombieri, G. de Paoli, A. Cassol, and A. Immirzi, *Inorg. Chim. Acta*, 1976, **18**, L23; *J. Inorg. Nucl. Chem.*, 1978, **40**, 799.