

Truter M R. Structures of organic complexes with alkali metal ions.

Struct. Bond. 16:71-111, 1973.

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The paper reviewed the structures, mainly as determined by X-ray diffraction, of crystals containing organic molecules and alkali-metal cations, but not organometallic complexes. Half the references were to compounds that might be considered complexes by the criteria used for transition-metal ions, and the second half, to the newly discovered ionophores and their (inequivalent) complexes. [The SC7⁹ indicates that this paper has been cited in over 175 publications.]

Organic Cationic Crystals and Ionophores

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The review was written six years after I had started to work on the chemistry of alkali and alkaline earth metals. In 1966 there had been doubt about the existence of complexes of these metal ions. In the newly formed unit we had set out to try to explain, at the molecular level, how biological membranes could discriminate rapidly, isothermally and in the presence of water, between sodium and potassium. Following the logic of transition-metal chemistry, we had made lipid soluble complexes by using chelating or multidendate monoanions to give neutrality and additional ligands to provide coordinative saturation. The review covered the structures of these complexes, of adducts of salts, MX, with molecules containing oxygen and nitrogen as donor atoms, and of alkali-metal salts of small anionic molecules of biological interest.

There had been two major, unpredicted developments since 1966. One was the discovery in independent laboratories of antibiotics (mainly fungal metabolites) that had marked effects on alkali-metal cation transport in respiring cell fragments. The other was C.J. Pedersen's¹ solo syntheses of crown ethers, for which he shared the 1987 Nobel Prize

in chemistry. Several crown ethers allowed extraction of alkali-metal salts into nonpolar solvents. Fifty references covered comprehensively the crystal structures of complexes of natural and synthetic "ionophores." The latter comprised 10 structures of crowns and their complexes from our, and 7 from three other, laboratories plus 5 on the aza crowns and cryptate complexes, the first part of J.-M. Lehn's Nobel prizewinning work.²

Our original contribution to the crystallography of crowns began with those supplied by Pedersen, who spent three months in the unit in 1969 on his retirement. I chose the first because the stoichiometry was 3:2 dibenzo-18-crown-6:RbNCS. My collaborator for six months, David Bright, showed the crystals to contain 1:1 complexes and uncomplexed crown molecules that differed from the complexed ones only in conformation. This is one³ of our original papers cited almost as frequently as the review. We established the structures of other 1:1 and of 2:1 complexes; we also made new complexes with 1:2 stoichiometry and designed and synthesised new ligands, e.g., 10 isomers of tetramethyldibenzo-18-crown-6.

A comparable review was written nine years later.⁴ Host-guest chemistry and molecular recognition had developed broadly; metal cations constituted one class of guest, and with ionophores as hosts there were 346 references to the work of many laboratories, some with large teams. D.J. Cram, the third 1987 Nobel laureate in chemistry, thanked 200 co-workers.⁵ His preorganised and very strong complexing agents for lithium and sodium were only part of, and were developed relatively late in, his program.

I wrote in a period of anxiety. The future of the unit had been put in doubt by the death in December 1971 of its Honorary Director, Sir Ronald Nyholm.

The review was a success because it was timely, to the credit of J.D. Dunitz, who invited me to write it as one of four making a volume on "Alkali Metal Complexes." I received the Royal Society of Chemistry Award for Structural Chemistry for 1985. [Editor's note: The three Nobelists referenced above, who shared the 1987 Nobel Prize in chemistry, are the subject of a recent *Current Contents*⁹ essay.⁶ It describes their work in the field of organic synthesis of molecules that mimic biological processes.]

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2. Lehn J-M. Supramolecular chemistry—scope and perspectives. Molecules, supermolecules and molecular devices. *Angew. Chem. Int. Ed.* 17:89-112, 1988.
3. Bright D & Truter M R. Crystal structures of complexes between alkali-metal salts and cyclic polyethers. Part 1. Complex formed between rubidium sodium isothiocyanate and 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxocyclo-octadeca-2,11-diene ("dibenzo-18-crown-6"). *J. Chem. Soc. B* 1970:1544-50. (Cited 155 times.)
4. Hilgenfeld R & Saenger W. Structural chemistry of natural and synthetic ionophores and their complexes with cations. *Top. Curr. Chem.* 101:1-82, 1982. (Cited 40 times.)
5. Cram D J. The design of molecular hosts, guests, and their complexes. *Science* 240:760-7, 1988.
6. Garfield E. Work on molecules that mimic biological processes leads to 1987 Nobel Prize in chemistry for Jean-Marie Lehn, Charles J. Pedersen, and Donald J. Cram. *Current Contents* (15):3-9, 11 April 1988.

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