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INORGANIC COMPLEXES

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ABSTRACT

Selected papers from Session C_3 on compounds assigned as inorganic complexes are reviewed and discussed.

INTRODUCTION

Nine papers concerning inorganic complexes are reviewed. These include $Ru(bpy)_3X_2$ ($X = OH^-$, Cl^-, Br^-, I^-, ClO_4^-, IO_4, ReO_4^-, VO_3^-) and $R_nNH_{4-n}Cl$, alkylammonium hexachlorostannates, trimethyl- and triphenylsulphonium cyanometallates of the $M(CN)_5NO^{3-}$ type, $MO(NO_3)_2 \cdot nH_2O$ ($M = Zr$ or Hf) and $Zr_2O_3CO_3 \cdot nH_2O$, $Ni(X_2) \cdot (q\text{-MepyNO})_n \cdot xH_2O$ (C_2H_5OH), where $X = Cl^-$ or NCS^-, $2CO(NH_2)_2 \cdot 4Mg(NO_3)_2 \cdot 4H_2O$, $4CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ and their analogues, $NiNi(CN)_4 \cdot nH_2O$, $Ni(NH_3)_mNi(CN)_4 \cdot nH_2O$ and the true Hoffmann-type clathrates.

This varied series requires differentiation. One group belongs to the well defined inorganic complexes. Others may be assigned on the basis of the ligands as of either inorganic or organic character. Some inclusion compounds are also involved and a proposal for the definition of inclusion compounds is therefore also given for their better differentiation from simple and complex compounds.

For all the compounds the thermal degradation and stability were studied, leading to information on their properties, reaction mechanisms, thermodynamics and possible utilisation in all branches of chemistry.

DISCUSSION

The choice of contributions for poster session C_3 was probably made only from the point of view of complex chemistry and therefore it was named "Inorganic Complexes". Although all nine papers concerned involve in-

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organic complexes, they are a varied series of compounds with very fine but important differences between each of them.

Nowadays, as in classical complex chemistry, we can design complex compounds having at least one site with a coordination bond. The coordination bond or the donor–acceptor bond between a metal ion and a ligand (containing a lone pair of electrons) may exist in only one part of the compound, mainly in its anion or cation, but can also be present in both forms of ions, in which event there are stronger bonded units in the compound. In this sense the simplest complex compound is the hydrated or aquated ion alone. However, in addition to classical complexes these are also more complicated ones and almost all these complexes belonging to both inorganic and organic chemistry depending on their different individual components.

The classical ammonia ligands are present in alkylammonium chlorides, in $R_n(NH_{4-n})Cl$ [1], and in more complicated cation chloride salts such as alkylammoniumhexachlorostannates $(nC_pH_{2p}+1)_M(NH_{4-M})_2SnCl_6$, prepared by Kowalewska et al. of the University of Gdansk [2].

Further classical complexes with the nitrogen-containing ligands bipyridine and phenanthroline with ruthenium in the cations, $Ru(bpy)_3X_2$ ($X =$ OH, X^-, ClO_4^-, IO_4^-, ReO_4, VO_3), were discussed by Bujewski et al. of the Technical University of Gdansk [3].

More complicated secondary and tertiary onium cations combined anions containing mixed ligands in the form of trimethyl- and triphenylsulphonium cyano metallates of the $[M(CN)_5NO]^{3-}$ type were studied by Győryová and Mohai at the Šafarik University (Košice) and the Technical University of Veszprém. They elucidated the interactions between the cation and anion [4].

Carbonates and oxonitrates containing water molecules as ligands are also classical complexes, and have been studied in the form $[M_2O(OH)_2(NO_3)_x \cdot 3H_2O](NO_3)_{4-x}$ by Prozorovskaya et al. at Moscow State University [5].

Apart from its role in classical complex chemistry, the coordinative bond is also important in inclusion compounds [6]. An inclusion compound is formed from two components, host molecules being combined with a guest component, the bonds between them being hydrogen bonds, Van der Waals forces or other similar types of bonds. In hydrated forms of these compounds water molecules often form an inclusion in the host. The fact that the included guest species may be replaced by other compounds indicates that included water is the guest [7]. The guest (and also the host in all types of inclusion compounds) can be various organic or inorganic compounds. Sometimes the whole host component is constructed with coordination bonds [as in the original Hoffmann compound $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, in the Werner complex $M(B)_4X_2 \cdot yB$, etc.].

The bond between the included guest and the host (the host being usually in macrocyclic, layered or tubular form) has different strengths depending on the type, volume and polarity of the components. If their structure is known, they may be designed very precisely (e.g., the shape of areas in the host, the number of components). If the structure has not been solved, Weber and Josel [8] and Sopková [9] proposed the name host-guest complexes or compounds.

The group of tetracyano complexes forming the clathrates (their structure is known) are the opposite group to the classical simple complex compounds in inorganic chemistry. The host molecules alone represent strongly bonded complexes in the cation and the anion, the inclusion being formed by hydrogen bonds in combination with the Van der Waals forces, and here we should not merely consider them from the point of view of inorganic chemistry [10,11]. Some papers with such themes were therefore included also in the organic session [12,13].

Between these two extremes there are new complexes that do not belong to the inclusion compounds. However, some of them do show some signs at least of an adduct.

The amide complexes studied by Orlova et al. at the Kurnakov Institute in Moscow have urea or acetamide as ligands; but urea is a well known host [6]. The amides are combined with magnesium nitrate [14].

On heating complexes of the $Ni(NCS)_2(qMePyNO)_n \cdot xH_2O(C_2H_5OH)$ type, in the first step of its degradation the release of H_2O or C_2H_5OH occurs, and only then are ligands lost from the complex. According to Jóna and Jamnický, the compounds coordinate solvent molecules and the complex remains polymeric or dimeric. Another group of compounds undergo stereochemical changes between the individual polymeric forms [15].

Recently, analogous compounds to classical alkylammonium chloride complexes have been reported, e.g., tetraethylammonium fluoride hydrates $[(C_2H_5)_4N^+F^- \cdot 11H_2O]$ named [16] as clathrates.

Real clathrates of tetracyano complexes, $Ni(NH_3)_2Ni(CN)_4 \cdot nC_6H_5OH$, have been compared with the structures of analogous simpler and more complicated compounds. A series of compounds starting with $NiNi(CN)_4$ nH_2O were chosen and several kinds of molecules (H_2O and NH_3 as ligands, H_2O, C_6H_6 and C_6H_5OH as guests) were examined [10]. Reháková and Sopková [11] studied a model compound with the host containing NH_3 or H_2O as ligands (the latter also acting as the guest in different amounts, depending on the conditions of preparation) and for sorptive experiments the most favourable form was $Ni(NH_3)_mNi(CN)_4 \cdot nH_2O$ ($n \neq 0$) [17].

The thermal degradation and stability of all complex compounds of very different types have been studied. The products and intermediates have also been studied by other methods such as spectrophotometric, crystallographic, X-ray and magnetic measurements, by means of which all the compositions have been obtained or checked.

Kinetic and thermodynamic studies helped to follow [2] thermal dissociation of alkylammonium compounds up to the stage of total volatilization.

With proton-containing groups in compounds of Zr and Hf the dehydration enthalpies and entropies have been calculated [5]. A thermogravimetric study made it possible to elucidate the dependence of thermal stability on the character of the organic ligand [14]. The stoichiometry of the thermal decomposition influenced the stereochemical changes in nickel(II) complexes [15].

The changes undergone be the clathrate of tetracyano complexes on interaction with other compounds surrounding it help in differentiating the bond strength and the thermal stability of sorptive materials [10].

The solid "coordinatoclathrate" (a term coined because the clathrate character preveals against the coordinated bonds) also exists with very small amounts of intercalated water [17] and it is applicable as a sorptive material in all forms ($n \neq 0$).

The intermediates and final products of the thermal decomposition of bipyridineruthenium(II) complexes have been used as catalysts and photocatalysts and also in solar energy conversion [3].

The study of complex compounds of the $Mg(NO_3)_2$ with bonded amides helped in the preparation of agrochemical materials [14].

Recent theoretical studies of these compounds have provided useful knowledge about newly prepared materials, their reaction mechanisms, stereochemistry and their characteristic thermal stabilities, indicating future areas for the utilization of the very rapidly growing group of complexes, but not only made from inorganic materials.

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