Poster Session: Model Complexes of Biochemical Interest

R1

Do 5B-Element Homologues of Sulfonamides exist?

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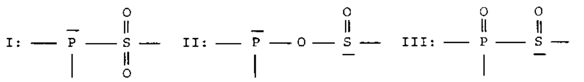
Sulfonamides are well-known and important substances. However the sulfonyl derivatives of the homologous 5B-elements are hitherto unknown because of the fast redox process for instance between phosphorus(III) and sulfur(VI). Now we have succeeded in their synthesis by metal coordination, where the complex fragment is acting as a protective group.

Results and Discussion

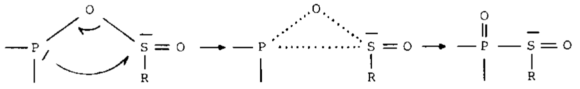
The ligand function of the ambidentate RSO_2-group to 5B-elements was initially investigated with respect to their graduated group properties. We have been successful in the synthesis and investigation of sulfinic derivatives of the type $R'_4E(O_2SR)$, $R'_3E(O_2SR)_2$ and $R'_2(O)P(O_2SR)$ with pentavalent 5B-elements or $E(O_2SR)_3$ and $R'_2E(O_2SR)$ with trivalent ones, by reacting the chlorides of the 5B-elements with silver sulfinates. They differ significantly in their physical and chemical properties (responsible for the reactivity pattern) as well as in their structures (ionic and covalent with linkage via one or two oxygen atoms and coordination numbers 3–5).

The 5B-element homologues of the sulfonamides with the formula $R'_2E(O_2SR)$ show the linkage via oxygen for E = As, Sb. In the case for E = P however we obtain – instead of the desired sulfonyl – phosphanes (I) or the sulfinylphosphinites (II) –only their tautomeric sulfinylphosphaneoxides (III) and only by the 'silyl method' (from trimethylsilyldiphenylphosphane and sulfonylchlorides):



$$\text{I: } -\underset{|}{\bar{P}}-\overset{O}{\underset{O}{\overset{\Vert}{\underset{\Vert}{S}}}}- \qquad \text{II: } -\underset{|}{\bar{P}}-O-\overset{O}{\overset{\Vert}{\underset{-}{S}}}- \qquad \text{III: } -\underset{|}{\overset{O}{\overset{\Vert}{P}}}-\overset{O}{\overset{\Vert}{\underset{-}{S}}}-$$

Thus we were successful in getting the desired phosphorus–sulfur bond, but at the cost of a synchronous tautomerization similar to the ' Arbusov–Michaelis reaction'. We also assume an intramolecular mechanism, where the oxygen linkage initially formed is rapidly tautomerized through a three-center transition state into the oxide:



'Analogous reactions were carried out with metal-coordinated functional phosphanes to avoid this 'Arbusov-like rearrangement' by blocking both the free coordination site and electron pair on phosphorus. Thus we obtain the metal-stabilized sulfinylphosphinites (O-isomer, II) with the so-called 'silver-salt method' or with the 'sulfinylation of metal-coordinated phosphinite anions'. But with the mild 'silyl method' a highly reactive sulfonylphosphane (S-isomer, I) can be finally synthesized for the first time, but only in the protecting coordination sphere of a metal:

$$[H(CO)_4Re-P(C_6H_5)_2O]^- + RSOCl \rightarrow$$
$$H(CO)_4Re-P(C_6H_5)_2(O_2SR) + Cl^-$$

$$L_nM-P(C_6H_5)_2X + YO_2SR \rightarrow$$
$$L_nM-P(C_6H_5)_2(O_2SR) + XY$$

$L_nM = BrMn(CO)_4, Cr(CO)_5, C_5H_5Mn(CO)_2$

$X = Cl, Si(CH_3)_3, Y = Ag, Cl$

R2

The Template Synthesis and Characterization of Ni(II) and Co(II) Perchlorate Complexes of Quadridentate Macrocyclic Ligand 2,5,11,14-Tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1.^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-Decaene

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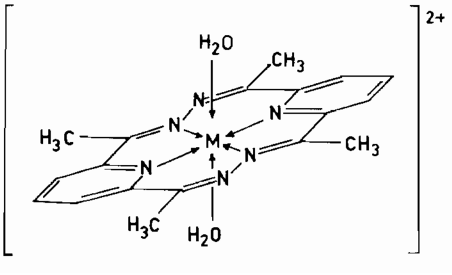
The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they may mimic naturally occurring macrocyclic molecules in their structural and functional features, and on their rich chemical behavior. Macrocyclic complexes with four nitrogen donor atoms have attracted considerable attention. Most macrocyclic ligand complexes are best prepared with the aid of metal ions as 'templates' to direct the steric course of the condensation reactions, which ultimately end with ring closure.

As a continuation of our studies on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocyclic compounds [1–5], we now report the template action of Ni(II) and Co(II) ions in the synthesis of a planar hexaaza quadridentate macrocycle. The free title ligand L has also been prepared without the aid of metal, albeit with very low yield [1].

The macrocyclic complexes of stoichiometry $[NiL(H_2O)_2](ClO_4)_2\cdot 4H_2O$ and $[CoL(H_2O)_2](ClO_4)_2\cdot 4H_2O$ were prepared by reacting 2,6-diacetylpyridine with hydrazine in the presence of metal salts with yields of 83 and 89% respectively. The formulations of these complexes follow from spectral data (i.r., uv–vis, e.s.r.) and thermal and elemental analyses. The infrared spectra of these complexes confirm the formation of the macrocyclic compounds by the absence of uncondensed functional group stretching modes of starting materials and the appearance of a strong absorption band at *ca.* 1600 cm^{-1} attributable to the coordinated C=N stretching mode. The high and low energy pyridine bands are observed at *ca.* 1570, 1460, 635, and 420 cm^{-1} suggesting coordination of pyridine. The presence of non-coordinated perchlorates in the complexes is inferred from the broad, intense band centered at 1100 cm^{-1} and a strong sharp band at 625 cm^{-1}, and also from the absence of splitting of the degenerate stretching and bending modes of ClO_4^- ion, which is indicative of coordinated species. A broad diffuse band in the 3500–3200 cm^{-1} region is assigned to O–H stretching modes for lattice water. A weak absorption observed at 530 cm^{-1} may suggest that coordinated water is also present. The electronic spectra of solutions of the complexes exhibit bands at *ca.* 37,000 and 280,000 cm^{-1}, attributable to the $\pi \rightarrow \pi^*$ transitions of the coordinated macrocycle. The electron spin resonance spectra of the cobalt complex taken in solution and in the solid state at room and liquid nitrogen temperatures give the value of g = 2.2, characteristic of low-spin complexes of Co(II) with square-planar or octahedral symmetry. The thermogravimetric analysis indicates for these two complexes loss of four molecules of water at 30–60 °C, and two water molecules at 120–160 °C.



On the basis of spectral and analytical data, along with the molecular model analysis, it seems reasonable to assume that these complexes have a six-coordinate octahedral structure with the macrocycle occupying the equatorial plane and the axial positions being filled with water. This structure is highly stabilized by the formation of two five- and two six-membered chelate rings upon coordination, which allows the high resonance of the system. The complexes satisfy the Hückel criterion having 14 π electrons in the inner ring and are therefore chemically stable and comparable in this regard with the derivatives of phthalocyanines and porphyrins.

1 W. Radecka-Paryzek, *Inorg. Chim. Acta, 34,* 5 (1979).
2 W. Radecka-Paryzek, *ibid., 35,* L349 (1979).
3 W. Radecka-Paryzek, *ibid., 45,* L147 (1980).
4 W. Radecka-Paryzek, *ibid., 52,* 265 (1981).
5 W. Radecka-Paryzek, *ibid., 54,* L251 (1981).

R3

EPR of Trigonal Bipyramidal Copper(II) Complexes with Tripod Ligands

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Very recent studies in one of our laboratories (KDK) have emphasized the usefulness of some tripod ligands in studying and modeling certain aspects of the coordination chemistry and structure properties of 5-coordinate copper(I) and copper(II) complexes [1]. Furthermore, the general features of the EPR spectra of 5-coordinate copper(II) complexes covering the full range from trigonal bipyramidal to square pyramidal are also now reasonably well understood [2]. In this paper we report the results of a single crystal and polycrystalline epr study of a well characterized complex: $[Cu(tmpa)X]PF_6$ with tmpa = tris (2-pyridyl)-methylamine and X = Cl^- (*1*) and a polycrystalline multifrequency (9–60 GHz) study of a related complex: $[Cu(tmpa)X]PF_6$ with X = N_3^- (*2*). The former material has a nearly trigonal bipyramidal geometry about a Cu(II) center and, of the 14 Cu(II) centers which lie within a radius 12 Å of one placed at an origin, 7 have their Z axes