ELSEVIER

Coordination Chemistry Reviews
154 (1996) 13–18

COORDINATION
CHEMISTRY
REVIEWS

The relative affinities of ligand atoms for acceptor molecules and ions: a long story revisited

Sten Ahrland

Inorganic Chemistry 1, Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden

Received 12 December 1995

One fine morning in June 1952, I was sitting at my desk in the Chemistry Building of Lund University, writing a report on the species formed in solutions of uranyl glycolate. The spring term was over and very few people were still around in the Inorganic Chemistry Department which, in fact, was not very densely populated even during the busier periods of the academic year. There was a knock at the door, and in stepped my friend Sture Fronaeus. He told me that a colleague of ours, Karl Johan Karman, assistant professor of organic chemistry, had just called. He had been asked by his friend Kai Arne Jensen in Copenhagen to arrange for a visit to Lund next day by two English chemists named Chatt and Wilkins. "These are inorganic chemists," Karl Johan had told Sture, "and I am in no position to entertain them, but I cannot possibly let my friend KA down. So I am looking for somebody who could take them on. Would you?" To Karl Johan's great relief, Sture promised at once to take care of the foreigners, realizing that this might be a good opportunity to make interesting acquaintances. Now Sture asked me to join him in entertaining the visitors. I gladly accepted the offer and a message was sent to K.A. Jensen. Next morning the two gentlemen, accompanied by their wives, arrived in Lund. We had a most interesting day, discussing the inorganic chemistry going on in Lund and in Welwyn, Herts, where it turned out that our guests were working in a laboratory run by ICI but nevertheless devoted to the pursuit of fundamental research. I also remember a pleasant break for lunch at the Grand Hotel where we were joined by the two ladies, and the conversation turned to the sights and amenities of Lund and Copenhagen, and other lighter matters. When we parted late in the afternoon Dr. Chatt rather abruptly asked whether he could possibly pay me another visit early next morning; he intended to go back to Copenhagen later in the day. I said that of course he was welcome; little did I think that I was heading for an interview that would strongly influence my future. Dr. Chatt duly arrived next morning, sat down in my visitor's chair and opened the conversation with the question: "Would you be interested in coming to work in our laboratory at Welwyn for a year?". I was a little taken aback, especially as I had realized the previous day that our subjects of investigation and methods of work were quite different. So I said that I feared that I had not much skill or experience to contribute in the field in which he was working.

PII S0010-8545(96)01249-0

But Dr. Chatt brushed this away by saying: "You know what I have done, but you don't know what I intend to do". Then he unfolded his plan to obtain a quantitative measure of the affinity of various exotic donor atoms, such as phosphorus and arsenic, with metal acceptors by measuring the stability constants of the complexes formed in solution. He believed that I was the man to do this; he would take care of the preparative work required. Of course, this sounded fine for a young man at the beginning of his scientific career, and so before we parted we had agreed to do our best to bring the project to fruition. As is so often the case, finances were the most tricky item, especially as I already had a family to care for. But on 30 December 1953 I set foot on English soil for the first time; my family followed later on. I was met at St Pancras Station by Dr. George Gamlen (who has now been Dean of the College of Science, Sultan Qaboos University, Muscat, Oman for many years). On New Year's Eve I entered the Inorganic Chemistry Department of the ICI laboratories at The Frythe, close to Welwyn Village, 40 km due north of Charing Cross.

I cannot resist giving a short description of this remarkable place. The main building was a Victorian mansion ("built in a not very fortunate period," to quote Dr. Chatt). During the Second World War the owners had rented it to the Government and moved to quieter quarters in the Republic of Ireland. I was told that the mansion had been used as a training center for agents of the Secret Service. Temporary accommodation had been erected all round the spacious grounds for various secret military schemes and for housing the people employed in these. After the War, the lease had been taken over by ICI which wanted a place to house laboratories devoted to long-range developments which were being created on the initiative of Sir Wallace Akers, at the time the company's very influential director of research. Sir Wallace firmly held that progress in pure science is the necessary foundation for innovative applied science. During my stay, the place was still called Butterwick Research Laboratories (after an originally proposed site), but afterwards they were very fittingly renamed the Akers Research Laboratories, in honour of their creator. Later, alas, other councils prevailed in top ICI circles, and so the laboratories were closed in 1962.

The Inorganic Chemistry Department was housed in a hut which had been devoted to the development of midget submarines; the large tank used for testing these devices was still in place beside the hut. Seldom has outstanding research taken place in more modest surroundings, at least not in the present century. The winter of 1954 had cold spells which made the almost non-existent heat insulation of the hut painfully evident. On Mondays we sometimes had to fight frozen water pipes. Personally, however, I escaped rather luckily. I pointed out that the standard temperature for the equilibrium measurements I was there to perform was 25 °C, and so a very small room, without windows, was set aside and thermostated for my benefit. I stayed there during the English winter, somewhat to the amusement of my hardier English colleagues but, I guess, to the envy of my Italian friend Luigi Venanzi (for many years Professor at ETH, Zürich) who had spent his early years in Libya. I remember that he caught very bad colds during his time at The Frythe.

The exotic donor atoms phosphorus and arsenic that had brought me to The Frythe posed several problems. Unlike the halide ions, they do not exist in solutions as monoatomic ions but always have to be used as phosphines and arsines, i.e. tied to other atoms which will influence their donor properties. In this respect they resemble nitrogen and oxygen, which are also present as donor atoms in ligands with some degree of complication. However, they differ from these by being much more susceptible to oxidation. Also, in the mid-1950s coordination chemistry in solution very much meant in aqueous solution. While many nitrogen and oxygen ligands are readily soluble in water, this is not generally the case with phosphines and arsines. Of course, Joseph Chatt knew that aromatic phosphines, unlike aliphatic phosphines, are reasonably stable in air. Furthermore, he had the idea of making them more water soluble by sulphonation of one or more of the aromatic rings. Among the acceptors known to react strongly with nitrogen group donors, we chose the silver ion for our measurements, as the silver electrode, when suitably pretreated, was known (not least from recent measurements by Ido Leden) to respond rapidly and precisely to the concentration of free silver ions in solution. It behaved in this way in the solutions under investigation, and thus we were able to determine quantitatively, for the first time, stability constants for complexes of this type. The complexes formed were very strong, particularly the first and third ones, AgL and AgL_3^{2-}. The second complex AgL_2^- had only a narrow range of existence and the fourth complex never formed even at the highest ligand concentrations available. This behaviour was completely different from what had been found at that time for silver complexes of other donor atoms including nitrogen. Generally, the second and fourth complexes dominated to such a degree, that Bjerrum [1] had assigned a "characteristic" coordination number of 2 and a maximum coordination number of 4 to the silver ion. Evidently, the silver–phosphine system displayed none of these traits. The preparation of the sulfonated arsine ligand was not achieved until I was about to leave The Frythe at the end of 1954. Fortunately, Norman Davies, arriving from Australia on sabbatical leave, was ready to take over the measurements. He found that arsine, although less acceptable to the silver ion than phosphine, still formed a strong first complex, but no further complexes could be produced in the fairly wide concentration range available. The range of existence of the first complex was even wider than that in the phosphine system. The considerably lower stability of the arsine complex (almost a factor of 10^3 in the value of the stability constant K_1) was a most important new fact; the assumption that complex formation followed a pattern very similar to that of phosphine already seemed natural at this stage [2].

Meanwhile, the investigation had been extended to sulfide and selenide donors of related composition. Here the heavier donor atom Se showed the higher affinity, although the difference between S and Se (about a factor of 10 in K_1) was much smaller than the difference in the other direction between P and As. Equally importantly, a maximum coordination number of 4 was readily attained, with no intermediate complex preferred [2].

A study of the phosphine and sulfide complexes of Cd^{2+} showed that these were very much weaker than the corresponding Ag^+ complexes; however, the phosphine was more stable than the corresponding amine [3].

Although at that time the results referred to above provided almost the only quantitative data bearing on the important question of the relative affinities of ligand atoms of group V and VI, we ventured a generalization. Joseph Chatt's extensive knowledge of the field, which allowed him to marshal a large amount of corroborative semiquantitative and qualitative evidence, combined with his remarkable intuition made this possible. We were also helped by the much more extensive data already available for the stabilities of halide complexes of a wide variety of metal ion acceptors. "Because all these things hang together", to quote a memorable statement of Joseph Chatt during one of our discussions of these questions.

The result, embodied in a review paper published in 1958 [4], was that acceptors could be divided in two groups (a) and (b). The (a) acceptors form their most stable complexes with the first donor atom of each group, i.e. with N, O and F, while the (b) acceptors form their most stable complexes with one of the heavier donor atoms, the position of which varies with the donor group. The actual affinity sequences are given in Table 1. Furthermore, the (b) acceptors are all situated in a triangular area of the periodic table, with its apex at copper.

It might fairly be stated that these far-reaching deductions have admirably stood the test of the time. As more experimental facts have been forthcoming, they have become ever more firmly established. In the 1960s, extensive investigations by Jannik Bjerrum, with numerous coworkers, in Copenhagen [5] and by Max Meier, working in Gerold Schwarzenbach's laboratory in Zürich [6], did much to confirm the conclusions stated in our review about the stabilities of the phosphine complexes, a particularly crucial question in this connection.

Furthermore, in 1963 Pearson made an important extension of the generalization to non-metallic acceptors [7,8]. In this connection the familiar terms "hard" and "soft" were coined for the acceptors of classes (a) and (b) respectively, as well as for the ligands they prefer. These terms refer primarily to the polarizability of the species concerned. However, it should be pointed out, that a high polarizability is certainly a necessary but by no means a sufficient condition for (b) behaviour. The outer electrons must also be at an energy level compatible with covalent bond formation; for metal ion acceptors this means a well-filled outer d-shell [9].

Although I never had the privilege of working directly with Joseph Chatt after 1958, my time at The Frythe strongly influenced much of my later work, including both calorimetric studies of complex formation in aqueous solution undertaken during the 1960s and later extensive investigations of the thermodynamics of such reactions in polar aprotic solvents [10].

Titration calorimeters allowing the rapid collection of accurate enthalpy data had been developed in the 1950s. The Thermochemistry Departments of Lund University

Table 1

Donor group	Oxidation state	(a)	(b)
VII	–I	$\mathrm{F} \gg \mathrm{Cl} > \mathrm{Br} > \mathrm{I}$	$\mathrm{F} \ll \mathrm{Cl} < \mathrm{Br} < \mathrm{I}$
VI	–II	$\mathrm{O} \gg \mathrm{S} > \mathrm{Se} > \mathrm{Te}$	$\mathrm{O} \ll \mathrm{S} < \mathrm{Se} \approx \mathrm{Te}$
V	–III	$\mathrm{N} \gg \mathrm{P} > \mathrm{As} > \mathrm{Sb} > \mathrm{Bi}$	$\mathrm{N} \ll \mathrm{P} > \mathrm{As} > \mathrm{Sb} > \mathrm{Bi}$

and Brigham Young University were particularly active in this field. We were neighbours of the former, which greatly facilitated our entry in the field; we were among the early arrivals. Quite soon a large body of thermodynamic data referring to complexes formed in aqueous solution, mostly involving metal ions as acceptors, had been accumulated. Surveys of the data available in the mid-1960s [11,12] showed that reactions between typically hard acceptors and donors are entropy controlled, i.e. are due to large gains of entropy, while the enthalpy changes are endothermic, i.e. unfavourable. In contrast, reactions between typically soft acceptors and donors are enthalpy controlled, i.e. exothermic, while the entropy terms are unfavourable, often very strongly so. These conditions could be interpreted in terms of differences in bonding and solvation of the species involved in the two types of interaction. In the hard–hard interactions, the dehydration of the strongly hydrated acceptor ions and ligands result in a large increase of entropy but consumes much energy. In contrast, the soft–soft interactions the reacting species are only weakly hydrated; therefore, their dehydration, does not cause a large increase of entropy nor does it consume much energy. However, the formation of a strong covalent bond is likely to release a large amount of energy. Thus the net result would be the strongly exothermic reactions with unfavourable entropy terms observed in these cases. Later, this interpretation was further substantiated by studies of the thermodynamics of the consecutive steps taking place in various complex systems [13].

Evidently, an even better insight into the interplay between solvation and complex formation could be gained by extending the measurements to solvents of different affinities to the acceptors and donors offered. Therefore, such a study was undertaken. In an effort extending over 20 years, and involving many enthusiastic and skillful coworkers, numerous complex systems were investigated in dimethylsulfoxide acetonitrile, pyridine and tetrahydrothiophene. The results fully confirmed the predictions stated above. Furthermore, these polar aprotic solvents were very favourable for the investigation of complexes formed by group V donors. Phosphines, arsines, stibines and bismuthines are readily soluble in these solvents; in contrast with water, no special treatment of the ligand is necessary in order to achieve a sufficiently high solubility. Moreover, typically soft acceptors such as Cu^+ and Au^+ are stable in these solvents and thus are readily available for investigation. Consequently, at last it was possible to confirm quantitatively the affinity sequence $N \ll P > As > Sb > Bi$ for soft acceptors (represented by Cu^+, Ag^+ and Au^+, of which the last is the archetypal soft acceptor) just 20 years after it had been first proposed on the basis of the mixed evidence available in the mid-1950s [10].

These results of my meeting with Joseph Chatt on that fine June morning in 1952 beautifully illustrates the lasting influence that an original scientific idea can have on the works and lives of the people exposed to it. Of course, this influence was not confined to myself and my coworkers, but extended to many others interested in the fundamental chemical question of selective affinities, discussed since the days of Torbern Bergman [14]. Ralph Pearson, Jannik Bjerrum and Gerold Schwarzenbach have already been mentioned. Among many others who took an early and vivid interest in the new concepts, I should particularly include Harry Irving, Christian Klixbüll Jørgensen, Giles Klopman and Ronald Nyholm. However, a number of scientists were indifferent, or even hostile. A frequent objection was that our approach was not directly characterized by numbers; consequently only qualitative predictions were possible. To us, this limitation seemed natural considering the very wide scope of our classification. It could not reasonably be blamed for not providing quantitative data for any specific reaction. We felt that it was well justified as a useful ordering tool for the vast field of acid-base interactions. Later, however, it turned out that numerical scales of softness can indeed be constructed where different parameters vary in much the same way, and as expected from the chemical character of the acceptors and donors involved [12].

Looking back on the story told above, I am also struck by the decisive part played by chance in our lives. I was indeed fortunate to meet Joseph Chatt at the very right moment in my career so that I was able to profit fully from our happy collaboration, both at that time and in the future. I am very glad, and proud, to have worked with Joseph Chatt, a great scientist and also a true gentleman.

References

[1] J. Bjerrum, Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen, 1941.
[2] S. Ahrland, J. Chatt, N.R. Davies and A.A. Williams, J. Chem. Soc., (1958) 264, 276.
[3] S. Ahrland, J. Chatt, N.R. Davies and A.A. Williams, J. Chem. Soc., (1958) 1403.
[4] S. Ahrland, J. Chatt and N.R. Davies, Q. Rev. Chem. Soc., 12 (1958) 265.
[5] J.C. Chang and J. Bjerrum, Acta Chem. Scand., 26 (1972) 815, and references cited therein.
[6] M. Meier, Phosphinokomplexe von Metallen, Dissertation 3988, ETH Zürich, 1967.
[7] R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 3533.
[8] R.G. Pearson (Ed.) Hard and Soft Acids and Bases. Dowden, Hutchinson and Ross, Stroudsburg, PA, 1973.
[9] S. Ahrland, Struct. Bonding, 1 (1966) 207.
[10] S. Ahrland, Rev. Inorg. Chem., 11 (1990) 195.
[11] S. Ahrland, Helv. Chim. Acta, 50 (1967) 306.
[12] S. Ahrland, Struct. Bonding, 5 (1968) 118.
[13] S. Ahrland, Struct. Bonding, 15 (1973) 167.
[14] T. Bergman, Nova Acta Regiae. Soc. Sci. Ups., 2 (1775) 159; see J.A. Schufle, Chymia, Vol 12 (Ed. H.M. Leicester), University of Pennsylvania Press, Philadelphia, PA, 1967.