ELSEVIER

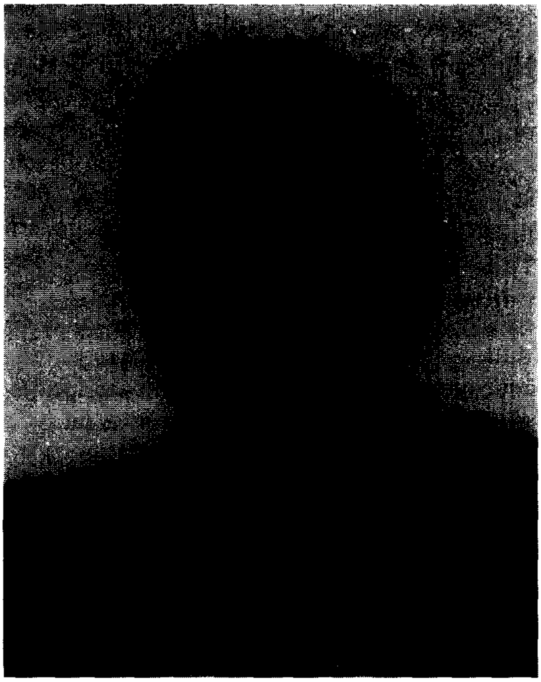
Coordination Chemistry Reviews
153 (1996) 1–23

COORDINATION CHEMISTRY REVIEWS

A celebration of inorganic lives: an interview with Sten Ahrland (Lund University, Sweden)

Lars I. Elding

Received 23 May 1995



Sten Ahrland is Emeritus Professor of Inorganic Chemistry at the University of Lund, Sweden. He was born in 1921 in Mariestad at Lake Vänern, and was educated at the University of Lund between 1940 and 1952, when he received his Ph.D. He was shortly thereafter appointed *docent* in Inorganic Chemistry. In 1954, he joined Joseph Chatt's team at the ICI Akers Research Laboratories in Welwyn, UK, and between 1958 and 1960 he was employed by the Eurochemic Co. in Mol, Belgium, as a section leader for the development of separation methods for fission products. He was a consultant to the Swedish Atomic Energy Co. between 1960 and 1970. He has been visiting scientist or professor at ETH Zürich in 1966, at the University of Copenhagen in 1974 and at the University of Rome in 1984. He was a research

SSDI 0010-8545(95)01181-1

fellow in Japan in 1982, and he has been a member of the IUPAC Commission on Equilibrium Data between 1969 and 1983, acting as its secretary (1973–81) and chairman (1981–83).

In 1960 Ahrland became an assistant research professor at Lund University, and in 1971 he received a personal appointment as Professor of Inorganic Solution Chemistry at the Swedish Natural Science Research Council, a position that he held at the Chemistry Department in Lund until 1982, when he succeeded Sture Fronaeus as Professor of Inorganic Chemistry. He retired as emeritus in 1987.

Ahrland is a member of the Royal Physiographical Society in Lund, serving as its permanent secretary from 1981 to 1995. He is also a member of the Danish Academy of Sciences and Letters, and a honorary member of the Italian Chemical Society. He received the Norblad–Ekstrand Gold Medal from the Swedish Chemical Society in 1965 and — for his work within the Royal Physiographical Society — the King's Medal in the ribbon of the Order of the Seraphim in 1994.

Ahrland's scientific contributions concern acceptor–donor reactions in solution. In the earlier investigations, for instance the doctoral thesis *On the complex chemistry of the uranyl ion* from 1952, the interest was focussed on the stabilities of complexes formed in aqueous solution. From such studies Ahrland developed, together with Chatt, affinity rules that formed the basis for the hard–soft acid–base concept. Further, when calorimetric measurements of heats of reactions were combined with stability data, it was evident that acid–base reactions of different types displayed different thermodynamic characteristics. To a large extent, these depend on the solvation of the species involved. The interplay with the solvent has been extensively investigated for acid–base reactions in solvents other than water. Finally, by combining the thermodynamic data with structural studies of the species present in solution, and of the solid phases crystallizing from solution, a fairly clear picture of the processes involved has emerged.

The scientific results have been reported in about 130 papers; one of them, written together with Chatt and Davies [1], has become a "citation classic" [2] (see also [3]). This paper has also been reprinted with comments by R. G. Pearson [4]. Ahrland has also contributed to handbooks and standard texts [5–9].

L.I.E. Sten — first perhaps a short account of your personal background. You grew up in a small town far from academic traditions?

Yes, there was no learned tradition in my family. My father had a business caring for the needs of the farmers around my native town Vänersborg, in the province of Västergötland. My paternal grandfather, a foreman in the engine maintenance shop of the State Railways in Göteborg, died when my father was 15. So my father had to start with practically two empty hands. My maternal grandfather started as a navvy, building the western Swedish part of the Stockholm–Kristiania (now Oslo) trunk line. When the line had been completed he stayed in the service of the railway and was soon promoted to engine driver. He even drove the royal train when King Oscar II travelled between his two capitals; Sweden and Norway were at that time in a union. Unfortunately, he fell ill and had to take early retirement; when he died, the family was left in very restricted circumstances. Further back, my forefathers were, as far as I know, tilling the soil as small farmers in Västergötland and Värmland. A typical Scandinavian ancestry, certainly.

So none of my parents had the economic means for a higher education, which had been a disappointment to them both. But they decided quite early that their children should fare better. In 1924, my parents decided to take over a small declining business in Vänersborg. One important consideration then was that the town, as the seat of the Provincial Governor, had a "Gymnasium" preparing for university studies. Real forethought, as I was only three and my brother less than one year old at the time. Still, we both used the facility in due course. Meanwhile, by hard work and thrift, my parents had brought their business into such a shape that they could support a university education once I was through the Gymnasium in 1940. I remember my father saying, when I had donned the white cap signifying that I had been duly approved in the examination, "Now we hope that you will in due time get a hat", referring to the doctor's hat that is part of the insignia for that degree at Swedish universities. As we were in quite a large gathering, my dear mother became rather embarrassed by my father's hubris, but no doubt she nourished the same hope herself. I am glad to state that they both lived to see it fulfilled.

L.I.E. I know that you are interested in many various subjects. Why did you choose chemistry? And why the University in Lund?

I was interested early in the wonders of Nature. Once I had entered the Gymnasium, the interest was more and more focussed on chemistry. I remember that I became fascinated by the law and order expressed by the periodic system. After school, I told my parents, "In the fall I am going to Lund to study chemistry". They did not object, my father only said, "How much do you think you want a month?" I mentioned a reasonable sum. My father replied, "That is about what I have come to".

I had two reasons for preferring Lund to Uppsala: living in Lund was considerably cheaper, and I had relatives in Malmö who could find me a good room in advance. Practically all student accomodation in Lund at that time was rented privately. The chemistry laboratories in Lund went on between 8 a.m. and 6 p.m. five days a week, with one hour off for lunch. In the evenings the students were expected to exercise solving chemistry problems. Saturday mornings there was a preparatory course in mathematics. It was indeed a hard schedule, but it had the advantage that almost everything I have had to tackle afterwards has seemed fairly easy.

After the first year I was drafted by the army to be trained in protection against gas warfare. In spite of the war going on beyond every Swedish border, however, most of my military training was postponed until my first degree was practically completed. Besides chemistry, I took physics, astronomy and mathematics. When returning from military service in 1944, I had decided to take up postgraduate studies in chemistry. Of the two branches then existing in Lund, my previous experience led me to choose inorganic and physical chemistry before organic chemistry. Also, the inorganic chemistry department had a position free as junior teaching assistant; very poorly paid, of course, but still paid.

Certainly, the chemistry of Uppsala at that time was of greater fame than that of Lund, with renowned scientists as The Svedberg, Arne Tiselius, Gunnar Hägg and

Arne Fredga. But during my years in Lund I had become so well rooted in this southern university that I never contemplated a move. This feeling has indeed grown even stronger over the years. Moreover, the Lund chemistry has meanwhile advanced to a state not second to that of Uppsala.

In fact, working conditions at the inorganic chemistry department of Lund in the forties and fifties were not at all bad, provided you were prepared to stand very much on your own. We had plenty of space and always money enough for what we needed (which was, in our line of research, not very much). We also had very skilled and resourceful instrument makers. The department had a fine experimental and theoretical tradition, essentially introduced by Ido Leden (who had already left when I entered) and further developed by Sture Fronaeus. It was presumed, however, that once you had been given a subject for your study, and some broad hints about literature and methods, you should conduct your investigation according to your own ideas and abilities. Supervision was hardly given, nor expected. Exceptions might occur in cases where no progress had been reported for a long time.

L.I.E. You started your Ph.D. work on uranyl complexes in the fall of 1944. How did you come across that subject?

The head of the department, Professor Sven Bodforss said, "We have brought together a lot of apparatus for the measurement of light absorption, to be used for determination of equilibria in coloured solutions. Uranyl salts are nicely coloured. I added chloride to an uranyl nitrate solution in a test tube once, and I think it turned more deeply yellow. You could try that". So the theme of my thesis was given. Rather few such determinations had been carried out earlier, and most of them had been interpreted in a rather questionable way. But Jannik Bjerrum in Copenhagen, and Harald Olerup in Lund, had recently devised adequate calculation procedures by use of the so-called "method of corresponding solutions". So I set out henceforth to measure colour changes occurring on the addition of various ligands to uranyl solutions.

L.I.E. I guess that neither Bodforss nor you, when you started that work, had any idea that actinide chemistry would become a very hot subject in the near future?

No, the Hiroshima bomb in 1945 turned uranium chemistry, until then a rather marginal topic, at least in peaceful Sweden, into a very important one. I found myself in demand both by the military and by the Atomic Energy Commission, and later on by other bodies engaged in the development of what is now called nuclear energy. As a consequence, I have worked part-time in actinide chemistry for most of my career. Until 1970, this was mainly experimental work within solution chemistry, in later years it turned to the writing of reviews for various handbooks, including Gmelin [5] and the extensive treatise *Chemistry of the Actinide Elements* [7].

L.I.E. Perhaps we could come back to your more applied actinide work later. Let us first consider your thesis and the conclusions drawn from that work.

I defended my thesis in the spring of 1952. It turned out that stability constants of the uranyl complexes formed in solution could be determined by the spectrophotometric method employed. Moreover, for those systems where the values could be checked by means of pH measurements, using quinhydrone or glass electrodes, the results agreed quite nicely, to our great satisfaction. This was an important result at a time when the reliability of the methods employed was still very much in doubt. A not uncommon view was that the constants calculated might well be artefacts devoid of physical reality. Thus, Ido Leden's epoch-making thesis from 1943, on equilibria in aqueous solution between the cadmium(II) ion and a large variety of inorganic ligands, had been dismissed by one professor of chemistry as a "fine piece of calculation"; very ambiguous praise indeed. Now, if two methods based on essentially different postulates gave the same results, such an opinion could hardly be upheld.

The chloride complexes that Sven Bodforss had postulated from looking at his test tubes turned out to be very weak, and the bromide ones were even weaker. On the other hand, complexes formed by ligands coordinating via oxygen, such as acetate and other carboxylates, were fairly stable. From reports in the literature, it was moreover evident that uranyl formed quite stable complexes with fluoride. This affinity sequence between the halide ions was contrary to that found by Ido Leden for cadmium(II) and also known to exist for mercury(II). On the other hand, it had been found that iron(III) behaved like the uranyl ion. This difference seemed quite interesting, and as soon as my thesis had earned me a semi-permanent position as *Docent* (about equivalent to assistant professor), I set about, with Ragnar Larsson, looking closer into this, starting with the uranyl fluoride system. Sure enough, very stable complexes were formed, up to $UO_2F_4^{2-}$.

L.I.E. So now we get on to the affinity rules for complex formation reactions. Your cooperation with Joseph Chatt on this subject is well known. How was that initiated?

My first meeting with Joseph was indeed an unexpected event that completely changed my prospects and future. One fine morning in June 1952, I was sitting at my desk writing a report on the species formed in solutions of uranyl glycolate (where chelating stabilizes the complexes fairly strongly). The spring term was over and very few people were still around. A knock at the door, and in stepped my friend Sture Fronaeus. He told me that a colleague of ours, Karl Johan Karrman, 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 K.A. down. So I am trying to find somebody who could take them on. Would you?" To Karl Johan's great relief, Sture promised 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. I gladly accepted the offer, and a message went 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 Imperial Chemical Industries, 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 that day. I said he was of course welcome; little did I think that I was heading for a most remarkable interview.

Dr. Chatt duly arrived next morning, sat down in my visitor's chair and opened the conversation with the question: "Would you be interested to come 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 in the field he was working I feared I had not much skill or experience to contribute. But this Dr. Chatt brushed away by saying: "You know what I have done, but you don't know what I intend to do". And then he unfolded his plan to obtain a quantitative measure of the affinity of various exotic donor atoms, such as phosphorous and arsenic, to metal acceptors by measuring the stability constants of the complexes formed in solution. This, he felt, I could do; he would look after the preparative work involved. This sounded, of course, fine for a young man at the beginning of his scientific career, so before we parted we had agreed to do our best to realize the project. As is so often the case, the economics were the most tricky item. But on December 30, 1953, I set my feet on English soil for the first time; my family followed later on. I was met at St. Pancras Station by Dr. George Gamlen (now retired after many years as Dean of the College of Science, Sultan Qaboos University, Muscat, Oman). On New Year's Eve I entered the Inorganic Chemistry Department of the ICI laboratories at the Frythe, close to Welwyn village, 40 km 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 Joseph) (Fig. 1). The owning family had rented it to the government during the war and had moved to quieter quarters in the Republic of Ireland. The mansion had been, I was told, used as a training centre for agents of the Secret Service; all around on the spacious grounds, provisional huts had been erected for various secret war 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 the laboratories devoted to fundamental research, to be created on the initiative of Sir Wallace Akers, at the time the company's very influential director of research. Sir Wallace firmly held the opinion 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 Akers Research Laboratories, in honour of their creator. Later, alas, other counsels prevailed in the top ICI circles, 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 during the war (Fig. 2). The big tank used for testing these devices was still to be seen outside. Seldom, certainly, 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 practically non-existent heat insulation of the hut painfully evident. On Mondays, the water pipes were sometimes frozen. 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, so

Fig. 1. Summertime tea-break on the lawn outside the mansion (with one of the wartime huts attached).

Fig. 2. Inorganic Chemistry Building of the ICI Butterwick Research Laboratories in 1954, "the hut". Dr. Alan Williams, who performed our sulphonations, descending for a tea-break in the main building, "the Mansion".

a very small room, without windows, was set aside and thermostatted for my use. There I stayed 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 (now retired after many years as Gerold Schwarzenbach's successor 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.

L.I.E. And what about the chemistry of the phosphine and arsine complexes?

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 offered as phosphines and arsines, i.e. tied to other atoms which will influence their donor properties. In this respect they of course resemble nitrogen and oxygen, also usually present as donor atoms in more or less complicated ligands. They differ from these, however, by being much more susceptible to oxidation. Also, in the mid-fifties, coordination chemistry in solution very much meant in aqueous solution. While many nitrogen and oxygen ligands are readily soluble in water, such as, for example, the carboxylates used in my previous uranyl studies, this is generally not the case with phosphines and arsines. Joseph Chatt knew, of course, that aromatic phosphines, contrary to aliphatic ones, are reasonably stable in air; furthermore he had the idea of making them sufficiently water-soluble by sulphonation of one or more of the aromatic rings. The phosphine used was a monosulphonate, the arsine a trisulphonate. Among the acceptors known to react strongly with nitrogen-group donors, we chose the silver ion for our measurements, as the silver electrode, suitably pretreated, had been shown recently by Ido Leden to respond rapidly and precisely to the concentration of free silver ions in solution. It did so also in the present solutions, and we were thus able to determine quantitatively, for the first time, stability constants for complexes of this type.

The complexes formed were very strong. This applied in particular to the first and third ones, AgL and AgL_3^{2-}. The second complex, AgL_2^-, on the other hand, had only a narrow range of existence, and the fourth one never formed, even at the highest ligand concentrations available. This behaviour was of course 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 were dominant to such a degree that Jannik Bjerrum had ascribed to the silver ion a "characteristic" coordination number of two and a maximum coordination number of four. Evidently, the silver phosphine system displayed none of these traits. The preparation of the sulphonated arsine ligand was achieved only when I was about to leave the Frythe at the end of 1954. Fortunately, Norman Davies, arriving from Australia on a sabbatical leave, was ready to take over the measurements. He found that the arsine, though less palatable to the silver ion than the phosphine, still formed a strong first complex, but no further ones in the fairly wide concentration range available. The range of existence of the first complex was even wider than in the phosphine system. The considerably lower stability of the arsine complex, almost 10^3 in the value of the stability constant K_1, was a most important new fact; that the complex formation evidently followed a pattern very similar to that of the phosphine seemed at this stage already natural.

Meanwhile, the investigation had been extended to sulphide and selenide donors of related composition. The heavier donor atom Se showed the higher affinity, though the difference between S and Se (about ten in K_1) was much smaller than the difference in the other direction between P and As. Equally important, a maximum coordination number of four was readily attained, with no intermediate complex preferred in particular. A study of the phosphine and sulphide complexes of Cd^{2+} showed that these were very much weaker than the corresponding Ag^+ complexes; still, the phosphine was more stable than the corresponding amine.

Though at that time the results referred to above were almost the only quantitative ones bearing on the important question of the relative affinities of ligand atoms of Groups V and VI, we ventured a generalization. Joseph Chatt's extensive knowledge of the field, allowing him to marshal a lot of corroborative semi-quantitative and qualitative evidence, combined with a remarkable intuition, made this rather bold venture possible. We were also helped by a steady increase of data referring to halide complexes. "Because all these things hang together", to quote a memorable statement of Joseph during one of our sessions pondering these questions. Already during my stay at the Frythe, Ido Leden, working there in the summer of 1954, had shown that platinum(II), present as a Zeise complex, had the same affinity sequence to halide ions as mercury(II) and cadmium(II).

L.I.E. In 1955 you returned to Lund. How did you proceed with this project?

On my return to Lund I made a point of further increasing the quantity of halide data. In fact such measurements were continued over many years, up to the mid-seventies. They included acceptors behaving like cadmium(II), mercury(II) and platinum(II), namely bismuth(III) (investigated together with Ingmar Grenthe, now since many years Professor at the Royal Institute of Technology, Stockholm), thallium(III) (with Lars Johansson) and copper(I) (with James Rawsthorne, Bernt Tagesson and Dinko Tuhtar). Several acceptors behaving like iron(III) and uranyl(VI) were also studied; vanadyl(IV) and zirconium(IV) (with Bertil Norén) and neptunium(IV) and neptunyl(VI) (with Lars Brandt), and less typical, nickel(II), copper(II) and zinc(II) (with Kjell Rosengren).

L.I.E. In your "citation classic" from 1958 together with Chatt and Davies, you then systematized the stability data available so far.

Yes, based on the rather limited data at hand, we were able to state 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 in the periodic table, 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 system, with its apex at copper, as had already been pointed out in 1955 by Ido Leden and Joseph Chatt [10].

It might fairly be stated that these far-reaching deductions have admirably stood the test of time. As more experimental facts have been forthcoming, they have been more firmly established. In the 1960s, extensive investigations by Jannik Bjerrum with numerous co-workers in Copenhagen, and by Max Meier, working in Gerold

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	$\mathrm{O} \gg \mathrm{S} > \mathrm{Se} > \mathrm{Te}$	$\mathrm{O} \ll \mathrm{S} \leqslant \mathrm{Se} \sim \mathrm{Te}$
V	-III	$\mathrm{N} \gg \mathrm{P} > \mathrm{As} > \mathrm{Sb} > \mathrm{Bi}$	$\mathrm{N} \ll \mathrm{P} > \mathrm{As} > \mathrm{Sb} > \mathrm{Bi}$

Schwarzenbach's laboratory in Zürich, did much to confirm the predictions in our review about the stabilities of the phosphine complexes, an especially crucial question in this connexion.

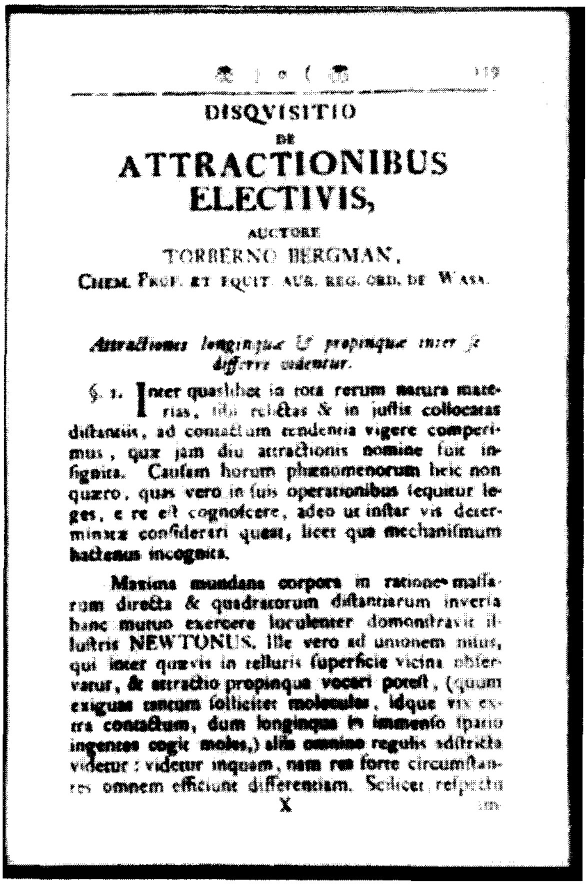
L.I.E. But the idea of two classes of acceptors must have been around even before your studies of the phosphine and arsine systems?

Of course, empirical affinity tables had been compiled earlier. The first systematic attempt was made by Torbern Bergman as early as 1775, embodied in his famous *Disqvisitio* [11] (Fig. 3). As far as metal complexes are concerned, the data on halide complexes before our work had already been extensive enough to allow the conclusion that two different affinity sequences existed. As early as 1943, in Leden's dissertation, there are hints to that effect; later on it had been noted by Jannik Bjerrum, Gerold Schwarzenbach, Göran Carleson and Harry Irving and, as described above, by myself, evidently all of us independent of each other. In the early fifties the idea was, so to say, in the air. But only the measurements involving donors of Groups V and VI made the more general classification possible.

L.I.E. In Sweden at that time, an appointment as docent lasted for six years. What happened after your docent period was finished?

My temporary appointment in Lund was definitely running out in 1959, and no other academic position seemed to be open. So when I was offered a position at the Eurochemic Co., situated in Mol, Belgium, in the spring of 1958, I readily accepted. As before, I was fortunate to have a family who did not hesitate to follow, in spite of the fact that Mol, in the heath country on the border between Belgium and the Netherlands, was not a really attractive place. The area was poor; still with much of the atmosphere immortalized by van Gogh in his painting *Ardappeleters* (The Potato-eaters), with the motif from his native village of Nuenen on the Dutch side of the border. A consolation was, however, the short distances to quite a few more interesting places, such as Brussels, Antwerp, Amsterdam, Aachen and, not least, the Mosel valley.

The company was a joint venture, with several European countries as partners, among them Sweden. Its purpose was to select and develop methods for the treatment of spent nuclear fuel. Our work was to result in the construction of a pilot plant for the separation of plutonium and fission products from uranium, essentially by liquid extraction, using tributylphosphate in a hydrocarbon diluent as extractant (known as the Purex process). This approach to the waste problem was at that time generally considered to be the most rational one; much process experience was also available from the separation of plutonium for military purposes. The technology is by no means simple, however. Its connexion with nuclear warfare also made it politically



119

DISQVISITIO
DE
ATTRACTIONIBUS
ELECTIVIS,
AUCTORE
TORBERNO BERGMAN,
CHEM. PROF. ET EQUIT. AUR. REG. ORD. DE WASA.

Attractiones longinquæ & propinquæ inter ſe differre videntur.

§. 1. Inter quaslibet in tota rerum natura materias, ubi relictas & in juſtis collocatas diſtantiis, ad contactum tendentia vigere comperimus, quæ jam diu attractionis nomine fuit inſignita. Cauſam horum phænomenorum heic non quæro, quas vero in ſuis operationibus ſequitur leges, e re eſt cognoſcere, adeo ut inſtar vis determinatæ conſiderari queat, licet qua mechaniſmum hactenus incognita.

Maxima mundana corpora in ratione maſſarum directa & quadratorum diſtantiarum inverſa hanc mutuo exercere luculenter demonſtravit illuſtris NEWTONUS. Ille vero ad unionem nitus, qui inter quævis in telluris ſuperficie vicina obſervatur, & attractio propinqua vocari poteſt, (quum exiguas tantum ſollicitet moleculas, idque vix extra contactum, dum longinqua in immenſo ſpatio ingentes cogit moles,) aliis omnino regulis adſtricta videtur: videtur inquam, nam rei forte circumſtantiæ omnem efficiunt differentiam. Scilicet reſpectu

X

Fig. 3. Title page of Torbern Bergman's (1735–84) famous thesis *Disquisitio de Attractionibus Electivis* of 1775 [11] where he states that, in addition to the general gravitation discovered by the "illustris Newtonius", there are also selective forces between various substances. Most probably this is the first time that the existence of what are now called electromagnetic bonding forces was recognized.

suspect. In most countries, among them Sweden, the authorities later yielded to the political pressure and settled for the solution of burying the untreated waste deep down, after a reasonable cooling-off time, though even now, in 1995, no final burial has actually taken place. A more elaborate treatment is, however, still practised in France, Britain and Japan. After all, simple burial demands a lot more space and, more important, involves a large waste of a potentially valuable energy source. It might well be, therefore, that a separation process will, after all, be preferred in the future. Fashion changes!

The pilot plant of Eurochemic in Mol was indeed built in the early sixties but, before it became operative, I returned to Lund in 1960, having been appointed Assistant Research Professor. This position really allowed a wholesale research effort. Part of that was devoted to nuclear chemistry, with the nuclear energy company, AB Atomenergi, as a sponsor. The project concerned separation of highly active nuclides by means of inorganic ion-exchangers, primarily zirconium phosphates. Contrary to organic ion-exchangers, these stand irradiation extremely well. Jörgen Albertsson (now professor at Chalmer's University of Technology) played a prominent part in these studies. Quite interesting separations were achieved in the laboratory experiments; for various reasons the technique was, unfortunately, never applied on a larger scale. My main research was still centred around the problems of relative affinities.

L.I.E. Could you please describe the further development of the affinity concept?

The classification of acceptors as (a) or (b) was capable of important extensions. Thus, in 1963 Ralph Pearson extended it to a large number of organic acceptors. In this connexion he coined the nowadays familiar terms *hard* and *soft* for the acceptors we had termed (a) and (b); the donors they prefer were also named hard and soft, respectively. These terms referred to the fact that soft acceptors and donors are highly polarizable. This is not the whole story, however, since a high polarizability is not a sufficient condition for (b), or soft, behaviour.

These developments aroused increased interest in the nature of the coordinate bond. So Christian Klixbüll Jørgensen and R.F. Hudson in 1965 convened a symposium at the research establishment then run by the Cyanamid Corporation, at Cologny, Geneva, where this topic was discussed extensively. I presented a paper arguing that, at least for metal-ion acceptors, high polarizability is not enough for (b), i.e. soft, behaviour. Many d-electrons also have to be present. This observation was interpreted as an indication of covalent bonding, where easily displaced d-electrons, of the right energy level, also participated. At this time, Ralph Pearson had high polarizability as a very dominant factor. In the notes he handed out before his introductory lecture, he even had placed the highly polarizable Cs^+ among the soft acceptors, obviously very much against its chemical behaviour. This struck Gerold Schwarzenbach as so preposterous that, even before Ralph had started his talk, he loudly called out, "You still put Cs^+ in the wrong box!"

Soft acceptors and donors also generally have a low, or even zero, ionic charge. Within a group of acceptors, the soft character increases with the radius. This of course also strongly indicates essentially covalent bonding. Typically hard–hard interactions are, on the other hand, favoured by high charge densities on acceptor and donor, which strongly indicates an essentially electrostatic interaction. At this meeting, an interesting theoretical interpretation of the bonding taking place under different circumstances was also presented by Giles Klopman.

Among the lecturers, I vividly remember the old professor Kasimir Fajans, justly famous for his pioneering work in radiochemistry. He had taken the trouble to cross the Atlantic at his own expense to tell us that we were all wrong. I can still feel the embarrassed silence in the audience after he had finished his talk. Finally, Ralph Pearson asked, "Professor Fajans, do you believe at all in quantum theory?" I do not remember the answer, but I think it was not very clearly articulated. Professor Fajans had his very private theory, and he stuck to that. He was by no means alone in taking a hostile view of the new concept. A common objection was that softness and hardness could not be expressed by numbers: consequently, only qualitative predictions were possible. To us, this limitation seemed natural, considering the very wide scope of the classification. It could not reasonably be blamed for not providing quantitative data for any specific reaction. We felt 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 and hardness can indeed be constructed where different parameters vary in much the same way, and, moreover, as expected from the chemical character of the acceptors and donors involved. These various scales have given rise to a lot of discussion, and even a lot of argument, during the years. On the other hand, we enjoyed the support of quite a few prominent scientists. In addition to those already cited, I would like to mention Harry Irving, Arthur Martell and Ronald Nyholm.

L.I.E. In the sixties, Chemistry in Lund expanded quite considerably. The Lund Institute of Technology with a complete Faculty of Chemistry and Chemical Engineering was founded, and the Chemical Center was built. You applied for the new chair of Inorganic Chemistry at the Institute of Technology?

So I did, but just before I left for Geneva I received disagreeable news which had a great impact on my future. I had good reasons to believe that I would be appointed. But the selection board thought otherwise. The members were extremely impressed by the rapid development of computer methods for calculating various chemical parameters. The fact that I had not contributed to the development of computer programs was held against me, whereas the board had only a mild interest in the problems of chemical bonding that occupied me. In retrospect, one might note that our review from 1958 was to become a citation classic already by 1980, a sign of significance that no other scientific contribution considered by that selection board was ever accorded. In my later work I have naturally used computer calculations extensively (though, admittedly, without having ever written a program myself).

Understandably, I was at the time somewhat disappointed. In the end, however, the Natural Science Research Council provided me with a personal position. As I now had no special obligations at home, I decided to use my unexpected freedom abroad to the best advantage. As Gerold Schwarzenbach was, like myself, very much interested in the question of chemical bonding, it seemed to me that a stay with him at ETH in Zürich would be a valuable experience. I was very happy to learn at our meeting in Geneva that I would be most welcome.

As things have turned out afterwards, I am not sure that being rejected for that chair in Lund was indeed such a great misfortune. Developing the new department from scratch would have involved a lot of administrative work that I was, after all, spared. The position at the Research Council allowed a much more concentrated research effort, and my home department, headed by my friend Sture Fronaeus, provided me with all necessary facilities. My reputation was admittedly shaken in some circles at home, but the international scientific community did not care about these internal Swedish affairs. So, on balance, what happened may well have been a blessing in disguise.

L.I.E. You spent a year at ETH Zürich. How did you develop your ideas together with Schwarzenbach?

Gerold Schwarzenbach's efforts to develop a classification similar to that advanced by Joseph Chatt and me had been hampered by the lack of data for donor atoms of Groups V and VI. Now he and Max Meyer had started work on complexes formed between various metal ions and an aliphatic phosphine, made sufficiently water-soluble by the introduction of an alcoholic group. As expected, this phosphine turned out to be an even more powerful donor to soft acceptors than the aromatic one we had used. Both the affinities of soft acceptors, namely copper(I), silver(I), mercury(II), methylmercury(II), cadmium(II), and of hard ones, zinc(II) and cobalt(II), were measured. The overall results beautifully confirmed our earlier conclusions, as I have already mentioned.

So far, the reasoning about the nature of the coordinate bonding had been based entirely on equilibrium data. It was obvious, however, that a deeper understanding of the various processes involved demanded a knowledge of the contributions of the enthalpy and entropy changes to the stabilities. By the early sixties, the need for such data had been realized in several places. Provided the reactions are not too slow, the best way to obtain such data is to measure the enthalpy changes calorimetrically. The best accuracy is obtained if the stabilities are determined separately, e.g. by potentiometric measurements. By combining the enthalpy and free-energy changes, the entropy changes are derived. Suitable calorimeters had been developed, particularly in the Thermochemistry and Physical Chemistry Departments in Lund and at Brigham Young University, Provo, Utah. In Lund, Per Gerding, Ido Leden and Stig Sunner, together with the skilled instrument-maker Evert Hedenstierna, had modified the calorimeters so that titrations became feasible. At my departure from Lund, calorimetric studies of several systems were going on, initiated already in 1959 by Sture Fronaeus, and carried on by Ido Leden, Per Gerding, Ingmar Grenthe, Heikki Ots and Torsten Ryhl.

While in Zürich, I set out to scrutinize the enthalpy data available so far. They were still scarce and, for most systems, referring only to the first step. Nevertheless it was obvious that reactions between typically hard acceptors and donors are entropy-controlled, i.e. due to large gains of entropy, while the enthalpy changes are generally 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. From very restricted material — the hard–hard interactions of aluminium(III) and iron(III) with fluoride, and the soft–soft ones of mercury(II) with chloride and bromide — Ido Leden already ventured a similar conclusion in 1964 [12]. 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 ones, the dehydration of the strongly hydrated acceptor ions and ligands brings large increases of entropy, as the resulting complex, on account of the neutralization of charges, is much less strongly hydrated. The dehydration consumes much enthalpy, however, so the overall reaction is apt to be endothermic. In the soft–soft interactions, on the other hand, the reacting species are only weakly hydrated; their dehydration, therefore, does not bring any large increase of entropy, nor does it consume much enthalpy. The formation of a strong covalent bond is apt to release much enthalpy, however. The net result would thus be the strongly exothermic reactions with unfavourable entropy terms observed in soft–soft cases.

For the few systems where the thermodynamics of the consecutive steps had already been determined by then, anomalous changes in the enthalpy and entropy values for certain steps were often encountered. Thus for the cadmium(II) halide systems studied by Leden and Gerding, the entropy change for the third step was abnormally favourable. I felt this might be interpreted as indicating a switch of coordination from octahedral to tetrahedral at that step, as such a switch should be accompanied by an especially extensive dehydration, causing an extra entropy gain. Gerold Schwarzenbach thought I was right, but added, "I do not think you will be able to convince the non-believers; they want a larger effect than that found here". This prompted me to think about which processes apart from dehydration might influence the observed net entropy changes. It struck me that the water molecules set free by dehydration of acceptors and donors do not really stay free. They become part of the fairly well-ordered bulk water structure. This must mean a severe decrease of the overall entropy gain. In less well-ordered media, therefore, the entropy terms should be larger and hence more clearly indicate what is happening at the interaction between acceptor and donor. On the other hand, these less-ordered media must still possess strongly solvating properties if charged species are allowed in them at all. I decided to explore this possibility, encouraged by the fact that at least stability measurements had, to a limited extent, been performed in such media. I had especially been impressed by the studies of Luehrs, Iwamoto and Kleinberg on silver halides in non-aqueous solvents of various donor properties [13].

L.I.E. How did you then proceed to further elucidate the thermodynamics of the stepwise complex formation having returned to Lund?

First, a number of suitably chosen systems should be investigated in aqueous solution in order to get a more comprehensive view of the conditions in the most important of protic solvents. Secondly, such measurements should be extended to aprotic solvents of marked donor properties where no hydrogen bonding exists while the solvation is still strong. On my return from Zürich, by use of calorimeters built according to the well-proven principles applied in Lund, the thermodynamics of numerous systems in aqueous solution were measured, including both hard–hard and soft–soft interactions. The results confirmed our assumptions beautifully. Lennart Kullberg (now professor at Winthrop University, South Carolina, USA) and Efraim Avsar (now Dean of the Science Faculty, Afalýa University, Turkey) contributed much to these studies, as well as to the following ones concerning aprotic solvents.

Besides good solvating ability, the aprotic solvents employed must also possess some other properties in order to be useful in practice. Quite important, they must be reasonably stable against oxidation and reduction. They must also have a suitable liquid range and be easy to get in a pure state. Further, they must dissolve an inert salt to a concentration high enough to provide an ionic medium for the potentiometric stability measurements wanted. It seemed advisable to start with a solvent coordinating via the hard donor atom oxygen, and then to go on to solvents coordinating via softer donor atoms, such as nitrogen and sulphur.

Dimethylsulphoxide (DMSO) was found to be an oxygen donor solvent fullfilling all the necessary conditions. As recent thermodynamic measurements in aqueous solution had generally been performed in ionic media with perchlorate as the non-complexing anion, it seemed natural to choose perchlorate media also in the aprotic solvents, and solid metal solvates were crystallized as perchlorates. In some instances, this led to very exciting incidents. Thus, when quite a small crystal of a silver(I) solvate was treated with a pestle by Nils-Olof Björk, who wanted a tiny sample for an X-ray structure investigation, a violent explosion occurred, leaving only the handle of the pestle left in the (fortunately not harmed) hand of the surprised investigator. Undaunted, however, he fished out a smaller crystal, and the ensuing structure determination [14] indeed gave a good explanation for the bad behaviour observed. A chain compound is formed where the silver atoms are joined by double bridges, provided by the oxygen atoms of the DMSO molecules. The innocent-looking stoichiometric formula $Ag(DMSO)_2ClO_4$ thus hides a sinister structure, prone to sudden decay. Several years later, Ingmar Persson one day called out that an odd-looking compound was precipitating from a silver DMSO solution he was just handling. I immediately recognized the bad guy and had him disappear as quickly as possible down the drain, accompanied by a lot of water.

We were especially interested in the DMSO hexasolvate of mercury(II) as we (rightly) suspected it to have a regular octahedral coordination, until then an unknown feature for mercury(II) compounds. Following earlier references, we precipitated the solvate from an ethanolic solution; its composition did not fit the hexasolvate formula very well, however. Meanwhile, news about these experiments reached Georg Johansson in Stockholm, who immediately warned us that a sample of the mercury(II) DMSO hexasolvate, prepared just in this way, had exploded after standing for some time in a desiccator. The explosion had caused considerable havoc in the laboratory; fortunately nobody was in when it happened. On closer investigation, we found in Lund that the instability was most probably due to a partial reduction of mercury(II) by ethanol during the preparation. Precipitation from non-reducing methanol, which only can be done at low temperatures — we used −78 °C; — as the solvate is readily soluble in methanol at room temperature, yielded a completely stable compound which analyzed exactly as a tetrasolvate. From this compound a pure hexasolvate was readily obtained. An X-ray structure determination by Magnus Sandström and Ingmar Persson in 1978 showed that this solvate indeed had the octahedral coordination postulated (though slightly distorted). I should mention that meanwhile another octahedral structure had been published; that of mercury(II) hexapyridine-*N*-oxide perchlorate. So we had to be content with having found the second one.

The first systems to be studied in DMSO were the cadmium(II) halides, in order to settle the questions already discussed. These were indeed crucial measurements, as they would decide the feasibility of the whole project. They turned out quite successfully, greatly due to the skilful work of Nils-Olof Björk (presently conducting the operations of the Heat Exchanger Division of the Tetra Laval Co. in the Far East). A step with an abnormally large entropy gain was found in all systems, and the values were, as foreseen, much higher than in the well-structured water. Further, it occurred already at the second step, as compared with the third step in water. A coordination change was then even more clearly indicated in DMSO; and it seemed quite reasonable that it should take place at an earlier step when ligands were invading the more bulky DMSO solvate.

L.I.E. You also observed a change of the affinity orders of the halide ligands when changing the solvent?

Yes, and that was a most important result of this study. The (b)-sequence in water was turned into an (a)-sequence in DMSO. An analogous change between protic and aprotic solvents had in fact been found for the silver(I) halides in the investigation already referred to [13]. The very marked (b)-sequence in the protic methanol is very much flattened in DMSO and other aprotic solvents. The explanation is evidently that not only solvent molecules but also electronegative ligands are hydrogen-bonded in protic solvents. This means that the strength of solvation increases more steeply from I^- to Cl^- in water than in DMSO. Consequently, the more electronegative the ligand, the more hampered is its complex formation in protic relative to aprotic solvents. Thus, the important general conclusion can be drawn that acceptors displaying very marked (b)-sequences in protic solvents will have these considerably evened out in aprotic ones; acceptors on the borderline will switch from (b) to (a), while acceptors with (a)-sequences in protic solvents will have these more marked in aprotic ones. Among the halide systems studied by us, the silver(I) and mercury(II) systems showed the first type of behaviour, the cadmium(II) systems the second, and the zinc(II) systems the third.

We paid special attention to the mercury(II) halides, as in these systems a strong second complex, with a very wide range of existence, is formed before further ligands are successively coordinated. This pattern was, of course, known from earlier studies in aqueous solution. We found it repeated in DMSO. For the soft acceptor mercury(II) we thought it would be especially interesting to extend the measurements to softer solvents. Acetonitrile (AN) and pyridine (Py) were found to work. Both coordinate via nitrogen, but the donor properties of Py are much stronger than those of AN. Consequently, much stronger complexes are formed in AN than in Py. The pattern of the complex formation is, however, the same as in water and DMSO. While in water the intermediate second complexes $HgBr_2$ and HgI_2 are only slightly soluble, the stronger solvation in the aprotic solvents, which was separately measured, made them easily soluble there.

L.I.E. There was obviously a strong need for structural studies of the solvates and complexes in the liquid phase?

Well, of course hardly anybody doubted that the zinc(II) and cadmium(II) solvates formed in solution were octahedral, but the question of the structure of the mercury(II) solvate was unsettled, since no solid octahedrally coordinated mercury(II) compound was known when our measurements were started. Meanwhile, however, the large-angle X-ray scattering (LAXS) method had been developed, not least by the Stockholm group headed by Georg Johansson, with Magnus Sandström as a co-worker, so that structures could also be determined in solution. From their measurements, partly performed in cooperation with members of our group, notably Ingmar Persson (now Professor at the Swedish Agricultural University, Uppsala), it was found that the solvates of mercury(II) are in fact octahedral both in water and DMSO. Already the first halide complex is, however, pseudolinear (with a DMSO trans to the halide), and so is the second one. On the other hand, the third complex is almost tetrahedral, with a solvent molecule in the fourth position. The fourth complex is, as expected, a regular tetrahedron. These structural changes are very compatible with the thermodynamics, which shows an extremely high entropy gain already at the first step.

L.I.E. But there must also have been complications due to the change of redox potentials and solubilities in the different solvents?

For the zinc-group metals, the redox conditions are not changed very drastically between protic and aprotic solvents. The divalent state stays predominant, and the equilibrium between mercury(II) and mercury(I) changes rather little between the various solvents. In this respect, the coinage metals present a very different picture. For copper, the monovalent state is stabilized very much relative to water already in DMSO; in Py and, even more, in AN it becomes predominant. Between water and AN, the value of the disproportionation constant $K_D = [Cu^{2+}]/[Cu^+]^2$ (M^{-1}) decreases by about 10^{27}! As in the case of mercury(II), the neutral halide complexes are soluble in all the aprotic solvents used. For copper, these include also tetrahydrothiophene (THT), coordinating via sulphur.

As to silver, the solvation of the neutral halides is not strong enough in DMSO or AN to make them soluble in these solvents; in Py and THT they are all readily soluble, however. Both Cu^+ and Ag^+ are tetrahedrally solvated in all the aprotic solvents used. For Cu^+ this has been determined by extended X-ray absorption fine structure (EXAFS) measurements, performed at SSRL at Stanford. We obtained access to this powerful tool through Henry Taube, with whom I had discussed these problems when we met in Jannik Bjerrum's Laboratory in Copenhagen in 1976. To get the samples half-way around the world took special precautions. Risk of breakage and explosion prevented us from bringing them in the registered luggage; even less did we dare to send them separately. We were also unwilling to put them in a carry-on bag, should it be searched and questions asked about poisons, etc. So in the end they travelled, well guarded, in Ingmar Persson's breast-pocket. With EXAFS, structure determinations can be performed also in dilute solutions, which is a great advantage as the conditions in the more concentrated solutions demanded by the LAXS method may be different from those prevailing in the dilute solutions employed in the thermodynamic studies. For Ag^+, the solvates were studied by LAXS, as EXAFS does not work for atomic numbers in that area. With halides, linear second complexes are formed in all the solvents used, the extensive desolvation being reflected in large gains of entropy.

Gold(I), which is extensively disproportionated in aqueous solutions, is very much stabilized in aprotic solvents; gold(III) is in fact not stable in these media. Thermodynamic studies were conducted in AN and Py. In both solvents, the halide formed complexes AuL_2^-, no doubt with a linear coordination. A striking fact is that the entropy gains in these reactions are very similar to those found on the formation of copper(I) and siver(I) complexes in the same solvents. We then concluded that Au^+ also forms tetrahedral solvates. As no tetrahedral gold(I) compounds were known, this conclusion might seem bold. To be really convincing, we wanted a direct structural proof. This was brought by EXAFS measurements. The Au–N distances in the AN and Py solvates in solution are indeed 0.2 Å longer than in the linear solvates formed in solid phases. This lengthening is just what is expected for a switch from linear to tetrahedral coordination.

The story just told illustrates that a combination of thermodynamic and structural measurements yields a much safer, and more extensive, knowledge than could possibly be gained by either type of measurement alone. On the other hand, structural information referring to conditions very different from those of the thermodynamic measurements must always be viewed with caution. This applies already to concentration differences in solution, and even more to solid phases crystallizing from the solutions. In such cases the activity conditions change so much that big surprises may be in store.

A very impressive case is presented by the crystalline solvates of copper(I), silver(I) and gold(I) iodide that can be obtained with THT. The stoichometric formulas are simple: $Cu(THT)_2I$, Ag(THT)I and Au(THT)I. The structures are not so simple, however. They are far from what might be presumed, and moreover very different. The copper(I) complex is a dimer, with the two Cu atoms joined by a double I-bridge. The silver(I) compound is a tetramer, with the four Ag in the corners of a regular tetrahedron. The Ag atoms are joined by four I atoms situated over the tetrahedral faces and forming an outer tetrahedron antiparallel to the first one. The fourth coordination site of each Ag atom is occupied by the S atom of a THT. The whole arrangement forms a symmetrical four-pointed star, a "stella quadrangula" (first recognized by Keplev as a possible spatial body of high symmetry). The gold(I) compound, finally, is an infinite chain of alternating cations $Au(THT)_2^+$ and anions AuI_2^-, joined by Au–Au bonds not much longer than in metallic gold.

This compound is also prepared in a way that clearly demonstrates the fundamental difference in chemistry between hard and soft donor solvents. Elemental iodine dissolves readily in THT; when gold foil is dipped into that solution, thin needles of the compound soon grow on the foil, even at room temperature. In the THT medium, metallic gold is thus rapidly oxidized to gold(I) by iodine under very mild conditions. Evidently, soft solvents open novel preparative routes of considerable interest.

These investigations of solvates and halide complexes in aprotic solvents would not have been possible without the whole-hearted cooperation of many skilful co-workers. Besides the contributions of Nils-Olof Björk, Ingmar Persson, Lennart Kullberg and Efraim Avsar, already referred to, I should acknowledge the fine work performed by Roberto Portanova (now professor at the University of Udine, Italy), Lennart Kullberg, Karin Nilsson, Bernt Tagesson, Dinko Tuhtar, Åke Oskarsson, Bertil Norén, Shin-ichi Ishiguro (now professor at the Technical University of Tokyo), Aurel Marton and Akio Yuchi, mentioned here in roughly the order they joined the project. For the work at SSRL, the cooperation of Britt Hedman, Keith Hodgson, and James Penner-Hahn has been invaluable.

L.I.E. You knew Jannik Bjerrum very well and spent a period as a visiting professor in Copenhagen in 1974?

Yes, I was invited to stay for a while in Jannik's laboratory at the H.C. Ørsted

Institute of Copenhagen University. I have already mentioned the extensive studies of stabilities of phosphine complexes in aqueous solution that had been conducted there for over a decade. Very stable complexes had been found for the soft acceptors copper(I), gold(I), mercury(II), palladium(II) and platinum(II), while little if any complex formation took place with hard acceptors such as cobalt(II), nickel(II) and zinc(II). These results were throughout compatible with those previously obtained by us at Akers, and by Meier in Zürich. Contemplating the programme for my Copenhagen visit, it struck me that the good solvent properties of DMSO, then in extensive use in Lund, might also very much ease the difficulties that had beset studies of the complexes formed by ligands coordinating via N, P, As, Sb and Bi. Indeed, it turned out that the simple triphenyl derivatives of all these donor atoms, as well as their complexes, are readily soluble in DMSO; unlike the case in water, no special treatment is needed in order to achieve sufficiently high solubility. We were able to determine the thermodynamics for the complexes formed by copper(I) and silver(I). As to the stabilities, it was possible, at long last, to confirm quantitatively the affinity sequence $N<P>As>Sb>Bi$ for soft acceptors, just twenty years after it had been first deduced from the mixed evidence available in the mid-fifties. Jannik Bjerrum was delighted. “DMSO is really a smart compound”, he exclaimed enthusiastically.

In connexion with these studies, we took the opportunity to introduce the Lund calorimeter model at the H.C. Ørsted Institute. The instrument, built in Lund, had to be transported across Öresund. To avoid all sorts of red tape at this transfer, I put it in the boot of my car when returning from a visit to Lund. Generally, my frequent appearences in the Tuborg harbour aroused no official interest, but this very time a young and ambitious customs officer felt that he should inspect my car. When discovering the calorimeter with auxiliaries, he exclaimed: “This must be valuable”. I explained that it was pieces of equipment that I was contributing to a joint venture that I, as a visiting professor at the Copenhagen University, was pursuing with very important people of that University. Evidently bewildered, he then chose to close the case (and the boot) and let me pass, though all the time repeating, “This must be very valuable...”

Some ten years later, we found in Lund that pyridine is also a good solvent for this purpose, though its stronger solvation makes the complexes much less stable. Even in this solvent, however, the very soft gold(I) forms very stable complexes, though not beyond the second one. The (b)-sequence is most marked, as befits this archetype among soft acceptors. As expected for these typical soft–soft interactions, complex formation is enthalpy-controlled. The entropies are generally unfavourable, often very much so, most probably on account of conformation difficulties. In these studies, Per Trinderup, Torsten Berg and Peter Bläuenstein, and later on, Felix Hulthén, Ingmar Persson and Stefania Balzamo all contributed beautifully.

L.I.E. Enthalpies of solvation are key parameters in the thermodynamic description of complex formation and solubility. What assumptions have you used in their determination?

Complex formation in solution may be looked upon as a competition between the solvent and the ligand for the coordination sites of the acceptor. Analogously, the solubility of a compound depends upon the forces of crystallization vs. those of solvation. For the outcome, the enthalpies of solvation of the various species are of major importance; a knowledge of these quantities lends much substance to the reasoning conducted here. The solvation enthalpies of neutral species can be found by adequate combinations of thermodynamic quantities. For ions, on the other hand, an extra thermodynamic assumption has to be introduced. Several have been proposed; in our studies we have applied the so-called TATB assumption as being, on the whole, the most reasonable one. This assumption presumes that the enthalpies, and entropies, of solvation are the same for the tetraphenylarsonium cation and the tetraphenylborate anion. In principle this approach was formulated by Ernest Grunwald, who, however, suggested the tetraphenylphosphonium ion as the cation to be employed.

Our measurements, which were extended to all the solvents used by us, confirmed very nicely all conclusions about the role of solvation inferred from the thermodynamics of the complex-formation reactions. An especially interesting result is that the enthalpies of solvation of the ligands XPh_3 ($X = N$, P, As, Sb, Bi) increase with the size of the donor atom. They are thus essentially determined by the induced dipoles, i.e. by the London forces, while the permanent dipoles are of little consequence. The sequence is opposite to that found for ionic ligands, e.g. the halide ions, where the enthalpies of solvation decrease with the radius, owing to decreasing charge density and, for protic solvents, also weaker hydrogen bonding. The heats of solvation of the uncharged ligands are also, very understandably, much lower than those of the ionic ones.

Our work on the thermodynamics in non-aqueous solutions has recently been summarized in a review [15].

L.I.E. You have also shown an interest in the chemistry of natural waters?

During the last 20 or so years, I have had the composition of natural waters as an interesting pastime. I was lured into the field by Paul Schindler, of the University of Bern, who asked me to write a review about metal complexes present in sea water, for a Dahlem Conference on the Nature of Sea Water, in West Berlin in 1975. The conference was certainly an interesting one, though the most stirring event was no doubt the passage of an East German train through this Western enclave. The train was pulled by an old-fashioned steam engine fuelled by brown coal. Everybody rushed to the windows, pressing their noses flat, to see this museum piece at work. For a prophetic mind, this sight might have foretold the coming collapse of the East German state. I afterwards returned to this important topic for an extensive IUPAC report [9]. In 1988, I further wrote a treatise comparing the conditions in the sea with those prevailing in saline lakes of different types. The differences, which are large, indeed reflect the geology of the various drainage areas, of course. This review was presented at a meeting at Primosten, on the Dalmatian coast. It is sad to know that this strange and beautiful land has since been ravaged by a cruel civil war.

L.I.E. You started your Ph.D. work fifty years ago. How would you summarize this long period of very active research?

"On the solid ground of Nature builds the mind that builds for aye", says a wise English poet. I agree. Progress depends on a wider and deeper understanding of

Nature. To achieve this goal, rational thinking, persistence and adequate tools are needed. That takes time and money. Understandably, there is always a temptation to spend these valuable and scarce assets on projects that promise a nice return quickly, i.e. on developing and modifying existing procedures and processes. It is in the nature of things, however, that new breakthroughs are not achieved in that way. For lasting progress, fundamental research is necessary; only if hitherto unknown lands are explored are really new things discovered. One has to accept, however, that a long time might lapse before fundamental discoveries can be turned into technical applications. It took almost one century to turn Ørsted's and Faraday's discoveries of electromagnetism and electromagnetic induction into the almost limitless supply of electric energy that we nowadays take for granted. The present astonishing state of electronics was not reached immediately upon J.J. Thomson's discovery of the electron. Everyone can add many more examples of fundamental research that in the long run have had a tremendous impact on our life or, if medical resarch is considered, on our (postponed) death.

But even if a fair share of the means available are set aside for fundamental research, the money is not always used in the wisest way. Many discussions about "priorities" and "relevance" tend to end up with a decision to jump on somebody else's bandwagon, instead of following a new path. Admittedly, there might be an immediate need for a crash programme to develop a field that is important and useful but has been neglected so far in, say, Sweden. But often, I have found that "relevance" is a matter of fashion. Joseph Chatt, Gerold Schwarzenbach and Jannik Bjerrum, all pioneers in important fields, have all told how little interest their work aroused in the beginning (of course, there were exceptions, both on the friendly and the hostile sides).

Among the most important tasks of those controlling the coffers is certainly to consider not only what is modern and relevant today, but also to find out what might be modern and relevant in a more or less distant future. Gazing into the crystal ball is, admittedly, not an easy art, but nevertheless it has to be tried. One might imagine that this gazing would be easier for the really outstanding scientists. Of course, this is often true. Exceptions are, on the other hand, not uncommon; eminence is by no means always combined with broad and far-sighted vision. Brilliant scientists might become so fascinated by their brilliant achievements that everything else disappears into the shadows. A well-known example is Nobel laureate Robert Woodward, whose efforts to keep Harvard free from improper brands of chemistry led to the ousting of a future Nobel laureate, Geoffrey Wilkinson, among others. In Britain, the predominant influence of Nobel laureate Sir Robert Robinson during the thirties and forties was certainly not to the advantage of contemporary inorganic chemistry, which was judged as rather devoid of interest. At an early stage of his career, Joseph Chatt was told by a prominent colleague that "your work on metal olefin complexes is of little interest to anybody". By an irony of fate, the later renaissance of inorganic chemistry was particularly vivid and spectacular just in Britain. It is easy to find earlier as well as more recent examples of such a restricted field of vision. Of course, everybody is entitled to his preferences; one should be aware, however, that the preferences of others might also be valuable.

I want to conclude these reminiscences by expressing once more my deep gratitude to all faithful friends, whose support has been invaluable, both in fair and in stormy weather. Some of them have, alas, left us for ever. As should be obvious from what I have told here, I have also had the good fortune to find many able and enthusiastic co-workers. I am deeply in their debt. Last, but certainly not least, I owe much to my wife Ingrid, who has been an untiring companion on a journey which has not always been easy.

My life has been devoted to the pursuit of science. I have never regretted that choice. It has indeed given me a full, and good, life.

To dare is to lose your foothold for a while;
Not to dare is to lose yourself
(Søren Kirkegaard).

References

[1] S. Ahrland, J. Chatt and N.R. Davies, The relative affinities of ligand atoms for acceptor molecules and ions, Quart. Rev. Chem. Soc., 12 (1958) 265.

[2] S. Ahrland, This week's citation classic (refers to ref. [1] above), Current Contents, 20 (1980) 24.

[3] A. Thackray (Ed.), Contemporary Classics in Physical, Chemical, and Earth Sciences, ISI Press, Philadelphia, 1986.

[4] R.G. Pearson (Ed.), Hard and Soft Acids and Bases, Dowden, Hutchinson and Ross, Stroudsburg, PA, 1973, in the series Benchmark Papers in Inorganic Chemistry.

[5a] S. Ahrland, Complex chemistry in solution: hydrolysis, in Gmelin Handbook of Inorganic Chemistry, Uranium, Supplement Vol. D1, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1984, p. 93.

[5b] S. Ahrland, Hydrolysis of thorium, in Gmelin Handbook of Inorganic Chemistry, Thorium, Supplement Vol. D1, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1988, p. 41.

[6] S. Ahrland, J.O. Liljenzin and J. Rydberg, Solution chemistry [of the actinides], in J.C. Bailar, H.J. Emeléus, R. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Vol. 5, Pergamon Press, Oxford, 1973, p. 465.

[7] S. Ahrland, Solution chemistry and kinetics of ionic reactions, in J.J. Katz, G.T. Seaborg and L.R. Morss (Eds.), The Chemistry of the Actinide Elements, Vol. 2, Chapman and Hall, London, 1986, p. 1480.

[8] S. Ahrland, Solvation and complex formation in protic and aprotic solvents, in J.J. Lagowski (Ed.), The Chemistry of Nonaqueous Solvents, Vol. V A, Academic Press, New York, 1978.

[9] S. Ahrland, Trace metal complexation by inorganic ligands in sea water, in T.S. West and H.W. Nürnberg (Eds.), The Determination of Trace Metals in Natural Waters, Blackwell Scientific Publications, Oxford (for International Union of Pure and Applied Chemistry), 1988, p. 233.

[10] I. Leden and J. Chatt, The stability constants of some platinous halide complexes, J. Chem. Soc., (1955) 2936.

[11] T. Bergman, Disqvisitio de attractionibus electivis, Nova Acta Regia Societatis Upsaliensis, 2 (1775) 159 (2nd ed., 1783).

[12] I. Leden, Pure Appl. Chem., 8 (1964) 171.

[13] D.C. Luehrs, R.I. Iwamoto and J. Kleinberg, Inorg. Chem. (1966) 201.

[14] N.-O. Björk and A. Cassel, Acta Chem. Scand. A, 30 (1976) 235.

[15] S. Ahrland, Rev. Inorg. Chem., 11 (1990) 195.