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A celebration of inorganic lives: interview with Lamberto Malatesta

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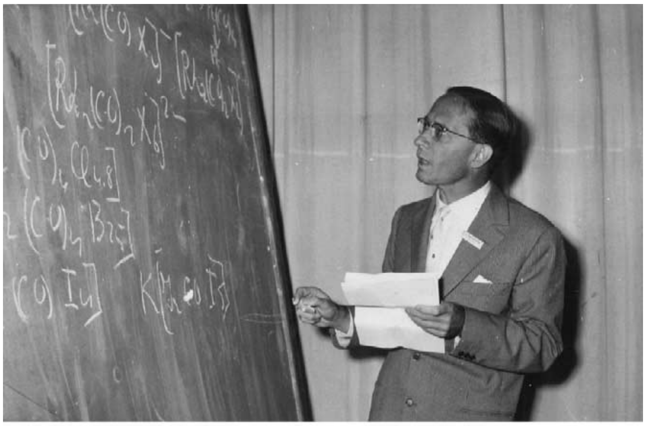

Lamberto Malatesta during a lecture in Muenchen.

Lamberto Malatesta was born in Milano in 1912 in a middle-class family originating from the north-eastern part of Italy. In 1948 Professor Malatesta was appointed to the chair of Analytical Chemistry of the University of Milano, and in 1951 to that of General and Inorganic Chemistry at the same university. Among his numerous research interests, specific mention should be made of the studies on isocyanide derivatives of transition metals in unusual oxidation states, on hydrido derivatives of iridium and rhenium, and on gold clusters. These studies led the way to still active and important areas of inorganic- and organometallic chemistry. He is a member of Accademia Nazionale dei Lincei and of Istituto Lombardo di Scienze e Lettere. He has been active within IUPAC for 23 years: first (1952–1969) as a member of the Committee for Inorganic Nomenclature, then as Secretary (1969), Vice-President (1971) and President (1973–1975) of the Division of Inorganic Chemistry. He has been a member of the Italian Consiglio Superiore di Sanità (Council for Public Health) and twice president of the Italian Chemical Society for the two terms of 1971–1974 and 1981–1983. He is Honorary Member of the Royal Society of Chemistry. He was a recipient of several national and international prizes, namely the prize of the President of the Italian Republic (1963), the Gold Medal of the Italian Ministry of Education (1973), the Gold Medal from Confindustria (Italian Federation of Chemical Industries, 1990), the Gold Medal of Società Chimica Italiana (Italian Chemical Society, in 1997), and more recently (2002) he was invited at the XXXth National Meeting of the Division of Inorganic Chemistry, Società Chimica Italiana, Modena, September 15–19, to give a plenary, successful, lecture based on his scientific achievements. Beside his scientific activity which will appear in the footnotes of the interview, Professor Malatesta has been author or co-author of a textbook of General Chemistry largely used within the Italian universities, and two monographs on “Isocyanide Compounds of Metals”, with F. Bonati, Interscience Monographs on Chemistry, and “Zerovalent Compounds of Metals”, with S. Cenini, Academic Press, London, 1974. Over the last 20 years he has collaborated with the scientific journal “La Chimica e l′ Industria”, for which he takes care of a periodical inset including highlights from the recent literature on Chemistry, Biochemistry and Geochemistry. He used to swim and to ski as a hobby, in more recent years he reads and actively plays bridge.

1. Could you tell us something about your education? What kind of high school did you attend ? How did you decide to begin your studies of Chemistry?

I attended the Classical High School “Giuseppe Parini” of Milan and the first elements of chemistry were provided by a teacher, who, in spite of having a degree in chemistry, did not appear to be well prepared on several aspects of the subject he was supposed to teach. Fortunately, I could take advantage

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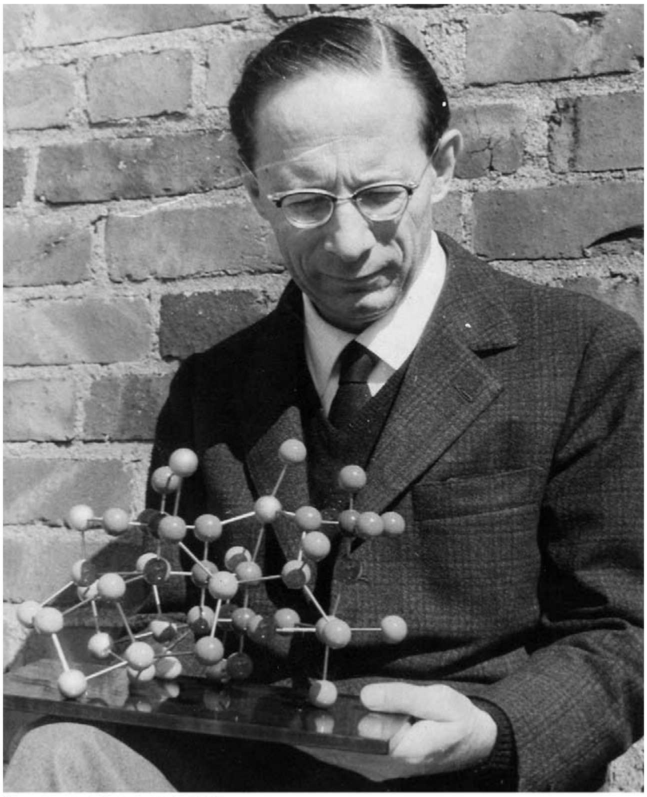
of my father who was managing at that time a small pharmaceutical company, and was able to overcome several deficiencies of my scholastic preparation. Immediately after the high school degree in July 1930, I spent about 4 months in London, to improve my English. After that, I enrolled at the University of Milan. The curriculum which I followed there to get the "laurea" of Industrial Chemistry, took place essentially in two institutes, that of General and Inorganic Chemistry headed by Professor G.R. Levi and that of Industrial Chemistry headed by Professor L. Cambi. The lectures of Electrochemistry, Chemical Plants and Unit Operations, Organic Chemistry, Physical Chemistry, Mathematics and Physics were delivered by teachers from other Institutes within the same University. My teacher of Physics, Giovanni Polvani, and those of Mathematics, Maria Pastori and Leo Finzi, later became colleagues of mine as members of the Accademia dei Lincei. The most difficult examination within the first biennial teaching was perhaps that of Qualitative Analysis, which required 300 h of laboratory training. The practical exam consisted of recognising, without specific reagents except dimethylglyoxime, a mixture of 8–10 inorganic salts including those of lithium, beryllium, strontium, vanadium, cerium, molybdenum, wolfram, thorium, and uranium. That teaching course, although excessive in terms of time, was extremely useful to open the entire world of Inorganic Chemistry to the young generation of students. The significant reduction in the number of such courses experienced in the most recent years almost all over the world, has certainly been unfavourable to the learning of Inorganic Chemistry. Incidentally, about 40 people began the first year courses, while at the end of the curriculum 17 were left, the selection being therefore quite high.

2. Is there any special event that you recall with particular pleasure? Which people have mostly contributed to your chemical education and whom you consider your scientific fathers?

Once my university curriculum terminated in 1935, I was employed as a volunteer ("assistente volontario") to assist Professor Cambi. Starting in 1937 I was in charge of the Quantitative Analysis course. My training in Inorganic Chemistry originated from Professor Cambi, who guided me towards his research in the field of the magnetic behaviour of transition metal xanthogenates and dithiocarbamates. I had the privilege to be excused from the military service, and, consequently, I was released from the draft, due to my strong short-sightedness. I could therefore carry on my scientific activity, during those difficult years between 1939 and 1945, in spite of the shortage of chemicals and scientific equipment. From this point starts my interest in Inorganic Chemistry.



Lamberto Malatesta in Milan

3. How did your scientific career develop?

In a series of articles which appeared between 1936 and 1940 I studied the chemical properties of dithiocarbamate and xanthogenate derivatives of iron, cobalt, nickel and chromium. These articles were published mostly in Gazzetta Chimica Italiana. However, some of the articles on iron dithiocarbamates were published in 1937 in Chemische Berichte which at that time was one of the most qualified chemical journals worldwide (this journal has recently disappeared, together with Gazzetta Chimica Italiana, and other prestigious European journals and merged into the new European Journal of Chemistry). In an article published in 1937 [1] the polymorphism of some iron dithiocarbamates was reported, together with the corresponding magnetic data. Professor Cambi had installed a magnetic balance in his laboratory, equipment which was really rare at that time in Italy; we could thus obtain some interesting results especially in the field of iron(III) dithiocarbamates which possess interesting magnetic behaviour as a function of temperature. It was therefore possible to establish that some of these compounds have a magnetic moment at room temperature corresponding to one unpaired electron, others, in spite of only a slightly different chemical constitution, have moments corresponding to five unpaired electrons, and some others have temperature-dependent magnetic moments. In this connection, it is important to realize that Professor Cambi had a good knowledge of the German language, and that article was written in German. Since Cambi had become, since 1925, member of the Accademia Nazionale dei Lincei (at that time named Reale Accademia d' Italia) and of Istituto Lombardo di Scienze e Lettere, a significant number of scientific results were published in the years of the war, in the Acts of those scientific institutions.

Around that time, I supervised the construction of an instrument for the determination of the dielectric constants of solutions; equipped with a variable condenser [2], I could start my own research on the molar dipole moment of several compounds, in order to study their structure. I could therefore determine the electric moment of some organometallic compounds, particularly tertiary and quaternary silanes [3,4] and of some tin derivatives [5]. These studies may be regarded as the starting point of my interests in organometallic compounds, particularly those of silicon, tin, lead and mercury. Besides I was interested in the chemical nature and possible applications of the esters of *ortho*-silicic acid which were prepared by a new way [6] starting from the sulfide SiS_2 [7]. The synthesis of the silicon esters was patented, beside being published [8]. An idea of the difficulties encountered in that period in carrying out our research may be given by considering that the basic chemicals at our disposal were limited substantially to benzene, bromine, chlorine, magnesium, the iron/silicon alloy, inorganic acids, ethanol, diethyl ether and a few inorganic salts. Therefore, during that time, the choice of any research was limited by the type and quantity of available chemicals and by the laboratory equipment. A good portion of these chemicals were provided to us by the Montecatini, at that time the leading chemical company in this country. In the course of these studies on the electric moment of nitrosyl derivatives, it was possible to show that NO bonded to a transition metal, at that time regarded as NO^+, is not the site of a positive charge, since its substitution with CO is accompanied by substantially no change of dipole moment. These studies on the dipole moment of inorganic substances, later attracted the attention of Dr. Joseph Chatt, who at that time was working at the research laboratories of Imperial Chemical Industries, and later became the leader of an inorganic team of outstanding value at the University of Sussex.

Lamberto Malatesta during a meeting in Milan.

4. What were the conditions of the Italian universities, and particularly that of Milan, at the end of the Second World War?

Throughout the whole of 1946, the situation in terms of availability of equipment for carrying out our research was literally tragic. I already noted the difficulties we encountered in obtaining the most basic chemicals; even worse was the fact that after 1939 we did not receive any scientific journals from English-speaking countries; we could only read the German journals, which, however, interrupted their publications in 1943. On top of that, several laboratories had been destroyed or damaged by bombing, including the chemical institutes of the University of Rome. After the war, considerable help came to us from the National Research Council (Consiglio Nazionale delle Ricerche, CNR), as well as indirectly from the USA, through the donation to Italian universities of scientific equipment, the so-called UNRRA (United Nations Relief and Rehabilitation Administration) Plan. Moreover, some of my research activity, especially that on metal carbonyls, was financed by NATO. Anyway, I was in a privileged position, with respect to many of my coeval colleagues, as I could publish a respectable number of scientific papers; thus, in 1947 I put myself forward for the appointment to a chair of General and Inorganic Chemistry and in January 1948 I was successful; I got a call to the chair of Analytical Chemistry at the University of Milan. This was the fourth chair within the curriculum of Industrial Chemistry within the University, the third chair being that of Chemical Plants, as assigned shortly before to Professor Gino Bozza. More than half of my scientific publications were without any coworkers, which shows how difficult it was at that time to have any help. Starting from 1948, after being appointed to the chair, I had a considerable number of very capable coworkers.

Lamberto Malatesta during a meeting of the IUPAC Committee, as President of the Division of Inorganic Chemistry(1973-5).

Due to my research activity on the dipole moment of inorganic compounds, published during the war, in 1949 I was invited by Dr. Chatt to visit him in Great Britain, thus initiating since then, a relationship of good friendship. The research laboratories of Imperial Chemical Industries were located at The Frythe, near Welwyn Village in Hertfordshire. Soon after, I have extended this friendly relationship to both Sir Ronald Nyholm and Sir Geoffrey Wilkinson. Both were very important actors in the development of Inorganic Chemistry in the United Kingdom at that time. In Italy, I believe that Luigi Sacconi and myself played such a role in those years.

In 1950 I was a recipient of a fellowship and I spent 3 months during the Summer at the Department of Chemistry and Radiation Laboratory of the University of California, where Glenn T. Seaborg had made his discoveries on transuranic elements, which resulted in him receiving the Nobel Prize in the following year 1951. In the same institution was the physicist Emilio Segré, who had received the Nobel Prize in Physics in 1959 for his demonstration of the existence of the antiproton. It was in fact through Professor Segré, born in Italy and a refugee in the USA before and during the war, that I obtained the invitation to attend the research laboratories of the University of California. At Berkeley, besides carrying out some research activity, I acquired a good knowledge in the field of radioactive elements and nuclear chemistry. I believe that this is an important part of Chemistry, and it is of interest to note that, 50 years later, in June 2001 I was invited to deliver a lecture on nuclear chemistry and on the cosmic formation of the elements at the University of Como.

Having the possibility to measure magnetic moments during the difficult years of the war, led me to use this technique in order to confirm the oxidation state of the central metal atom in some substances. This was particularly true for compounds in really unusual oxidation states. Thus, I had been able [9a,b] to confirm the presence of $\mathrm{Cu}^{\mathrm{III}}$ and $\mathrm{Ag}^{\mathrm{III}}$ in periodates and tellurates of these elements, which I had obtained in a pure state for the first time. These results were published in 1941, in the middle of wartime. The magnetic susceptibility measurements had shown that these compounds are diamagnetic containing the central metal atom in the $3d^8$ and $4d^8$ electronic configurations respectively, thus confirming the proposed oxidation state. Even nowadays, compounds of these cations in these oxidation states are limited in number, due to the difficulties connected with their synthesis. This may be noted from the fact that an excellent compendium of coordination chemistry [9a] and its recent revision [9b] still contains a relatively small number of references to derivatives of these metal cations. Also the study [10] of the so-called μ-peroxo $\mathrm{cobalt}^{\mathrm{III}}$–$\mathrm{cobalt}^{\mathrm{IV}}$ took great advantage from the magnetic susceptibility measurements as it was possible to show an electronic vacancy as indicated by the magnetic moment of about 1.7 BM, involving the two cobalt atoms and the oxygen atoms of the bridge. The magnetic susceptibility measurements were usually carried out at three different temperatures (373, 291, 96 K), corresponding to the boiling point of water, room temperature, and liquid nitrogen temperature, respectively.

Lamberto Malatesta shaking hands with Prof. Luigi Sacconi, 1976, during a IUPAC Meeting.

5. The first homoleptic derivative of an alkyl-isocyanide (of zerovalent nickel) was published in 1951 in Rendiconti Accademia Nazionale dei Lincei. This paper was signed by yourself and by Adriano Sacco. One year before, Professor Walter Hieber and his coworkers had reported the first aryl-isocyanide derivative of nickel, as obtained by carbonyl substitution from $Ni(CO)_4$. How did you get into this type of chemistry?

My interest in isocyanide complexes of transition metals originated from my reading a paper by Eastes and Nurgess published in 1942 [11a], which I could see only after the end of the war, for the reasons which have been already explained. In this paper the authors had described the compound K4[Ni(CN)4], which had interesting and surprising properties for that time, nickel being in the formal zero oxidation state, in spite of the ionic nature of that compound. On the other hand, Italian chemistry had a long-standing tradition in nickel–cyanide complexes, as already back in 1914 Bellucci and Corelli [11b] of the University of Roma had published a cyano-complex of nickel(I) as the potassium derivative $K_4[Ni_2(CN)_6]$, later structurally characterised [11c] to contain a nickel–nickel bond at a distance of 2.32 Å. By considering the similarity between CO and the CN^-, I therefore started wondering whether the electrically neutral isocyanides could also stabilise the low oxidation states of transition elements. Uncharged complexes should therefore result, amenable to measurements in organic solvents. Thus, in 1947 [11d–f] I was able to prepare some isocyanide complexes of bivalent cations, thus verifying the coordinating properties of these systems. The aryl- and alkyl-isocyanide complexes of transition elements represent an important point in the development of organometallic chemistry. This type of chemistry is simultaneous with and, for some aspects, prior to the correct bonding scheme for ferrocene by G. Wilkinson and coworkers and to the establishment of the structural features of the bis-arene derivatives of chromium(0) by E.O. Fischer and his coworkers. In collaboration with Adriano Sacco, the first tetra-alkylisocyanide derivatives of zerovalent nickel were published in 1951 [12a], obtained by treating salts of bivalent nickel with the ligand which acted both as the reducing and the complexing agent, or in the presence of a mild reducing agent. This paper was submitted for publication shortly after the article by Hieber and coworkers, who reported similar zerovalent derivatives of aromatic isocyanides, obtained by a different route, i.e. by carbonyl substitution from $Ni(CO)_4$ [12b]. With alkyl-isocyanides, Hieber's route led only to partial substitution of the carbonyl groups. This first paper of ours was followed by others, where we described the preparation and the properties of the isocyanide complexes of zerovalent chromium, molybdenum and wolfram. As the hexacarbonyls of these elements were not commercially available, and we had no high-pressure equipment for their preparation, we were further pressed to find an alternative route. Fortunately, we discovered that chromium(II) salts undergo disproportionation in the presence of isocyanides, leading to the required derivatives of chromium(0), $Cr(CNR)_6$. The synthesis of the molybdenum and tungsten derivatives was, however, more difficult and required the use of magnesium as the reducing agent. Another interesting target was obtaining the isocyanide derivatives of the elements of the nickel triad. Particularly interesting was the possibility to obtain the isocyanide derivatives of zerovalent palladium and platinum, whose carbonyl derivatives were unknown.

Fred Basolo, newly elected Honoray Member of Societa' Chimica Italiana (SCI) receives the parchment from Lamberto Malatesta, President of SCI. Meeting of SCI, Catania, Italy, September 1981.

The reducing power of the aryl isocyanides, combined with the action of alcoholic potassium hydroxide led to the synthesis of the isocyanide derivatives of palladium(0) of formula $Pd(CNR)_2$, and in the period from 1954 to 1956 also the first isocyanide complexes of zerovalent platinum were isolated [13]. These studies were followed by the publication of the isocyanide derivatives of cobalt(I), manganese(I), rhodium(I), and rhenium(I), formulated as $[Co(CNR)_5]X$, $[Mn(CNR)_5]X$, $[Rh(CNR)_4]X$, $[Re(CNR)_6]X$. These were among the first examples of derivatives of these elements in their +I oxidation state. The relevance of these findings is at the origin of the invitation by F.A. Cotton to write a chapter in the first volume of Progress in Inorganic Chemistry, published in 1954 [14a], further expanded to an entire volume, written together with my former student Flavio Bonati, further due to become professor at the University of Camerino [14b]. In this period are the preparations of several carbonyl-halo derivatives of transition metals, such as $[IrBr_2(CO)_2]^-$, $[IrBr_4(CO)_2]^-$, the first nitrosyl derivatives of iridium, and the hydrides $[ReH_5L_2]$, $[ReH_5L_3]$, and $[ReH_3L_2]$.

6. Are there other scientific observations which may be considered to be relevant for the development of this type of chemistry?

I believe that the isolation of the triarylphosphine derivatives of palladium(0) and platinum(0) may be regarded as an important step in the development of inorganic chemistry [14c]. These compounds of 4d and 5d metals had already been the object of our interest in the late fifties [15a]. The initial idea came by considering that it would be of interest to prepare phosphine derivatives of palladium(0), due to the limited number of compounds of that metal in the zero oxidation state existing at that time. Since the isocyanide derivatives of palladium(0) had already been prepared, the successful attempt was made to displace the isonitrile ligand with triarylphosphines [15a]. The substitution of the ligand in $Pd(CNR)_2$ by PR_3 (R = alkyl, aryl, OR) is immediate and give place to $Pd(PR_3)_4$. These compounds can also be easily obtained [15a] directly $[PdO + 5PR_3 \rightarrow Pd(PR_3)_4 + OPR_3]$. An analogous reaction allowed the preparation of the corresponding platinum(II) derivatives, which could not be obtained by substitution [15b]. The existence of these compounds was at that time so innovative that a major expert of inorganic chemistry such as Ronald Nyholm thought that these compounds could be better formulated as hydrido derivatives of the more conventional oxidation state +II of these elements, i.e. $MH_2(PAr_3)_4$, M = Pd, Pt. In a paper published with Ugo in 1963 [16] we could however demonstrate that our formulation was correct; on that occasion, we in fact synthesised also the true dihydrido derivatives. On the other hand, we had some experience with hydrido-triarylphosphine complexes of transition metals and in 1964 we had published some similar complexes of rhenium. Among my other research interests, I would like to mention the chemistry of cluster compounds, such as the anionic $[Ir_6(CO)_{15}]^-$ [17], an early example of a chemistry later extended and developed systematically by Chini and Longoni, and their coworkers [18]. Having obtained the phosphine derivatives of palladium(0) and platinum(0), and taking into consideration that gold forms a diatomic molecule with a respectable gold–gold bond enthalpy, it was reasonable to think that a molecule such as $R_3P–Au–Au–PR_3$ (cf. $R_3P–Au–X$) could have a sufficient stability to be isolated. Thus, several tertiary-phosphine complexes of gold(I) were subjected to reduction, but the hypothesised Au_2R_2 did not form. However, gold was never reduced to the metallic state but we obtained instead soluble products which were characterised as cluster compounds of gold, with the metal in a fractional oxidation state. Some of these clusters are ionic, other are non-ionic, for example $[Au_9L_8]^{3+}(X)_3{}^-$, $[Au_6L_6]^{2+}(X)_2{}^-$, $[Au_{11}L_3X_3]$. The structure of some of these products was established by X-ray diffraction methods [19]. This research on phosphine derivatives of gold has been pursued extensively elsewhere.


Lamberto Malatesta during his lecture, XXXth National Meeting of the Division of Inorganic Chemistry, SCI, Modena, September 15-19, 2002.

7. You have been nominated Emeritus Professor of the University of Milan. For a long while, you have been carrying out an appreciated activity in reviewing the scientific journals and publishing the corresponding highlights in “La Chimica e l′ Industria”. What is your opinion about the present scientific chemical production with respect to the situation of some decades ago?

My activity in the field of the peer-reviews began two decades ago; initially this was limited to Inorganic Chemistry and later was extended to other branches of Chemistry. In the most recent years scientific papers have come to deal with specialised studies, which may be followed only by a limited number of interested people. I believe that one should not forget that Chemistry is part of the scientific world, of great utility in other fields; for this reason, I have extended my literature survey to other branches of the natural sciences, particularly Biology and Physics, beside Medicine and Earth Sciences.


Lamberto Malatesta receives a commemorative plate from Luigi Busetto, Chairman of the Division of Inorganic Chemistry, SCI, XXXth National Meeting of the Division of Inorganic Chemistry, Modena, September 15-19, 2002.

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