

The First Chemical Achievements and Publications by Justus von Liebig (1803–1873) on Metal Fulminates and Some Further Developments in Metal Fulminates and Related Areas of Chemistry^[‡]

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Dedicated to Professor Wolfgang Steglich on the occasion of his 70th birthday for his great friendship, collaboration and support^[‡‡]

Keywords: Liebig / Fulminates / Silver / Structure elucidation

The first chemical investigations and publications by Justus von Liebig dealt with the fulminates of silver and mercury. Even as a boy Liebig had learnt how to prepare silver fulminate, and as student of chemistry in Erlangen (1821) he studied the properties and reactions of silver fulminate. In Paris in 1823 (together with Gay-Lussac) he succeeded in analyzing quantitatively the highly explosive silver compound. This great experimental success with the dangerous silver fulminate was most important in three respects: i. The development of the experimental method later culminated in Liebig's perfected and well-known C,H,N analysis of organic compounds (1830). ii. It led to the concept of isomerism when F. Wöhler found that silver cyanate had the same composition as silver fulminate. iii. It was decisive for furthering the scientific career of Liebig, since Alexander von Humboldt was highly impressed by the great skill and talent of Liebig and — by recommendation of Humboldt — Liebig became Professor in Gießen in 1824 (at the young age of 21). The first (fulminato)metal complex, $K[Ag(CNO)_2]$, was also isolated

by Liebig. Later, explosive (fulminato)metal complexes were prepared by Nef, Wieland, and especially by Lothar Wöhler and co-workers. In Munich the HCNO structure of fulminic acid was established by its IR spectrum and the spectroscopic properties of (fulminato)metal complexes were studied. A series of new nonexplosive complexes could be obtained by dilution of the energy-rich species with large cations or ligands. Recent X-ray structure determinations have revealed the almost perfect linear, tetrahedral, square-planar, or octahedral structures of these complexes with linear metal–C≡NO bonds, e.g. $[Au(CNO)_2]^-$, $[Zn(CNO)_4]^{2-}$, $[Ni(CNO)_4]^{2-}$, $[Co(CNO)_6]^{3-}$. DFT calculations have given very good agreement between the calculated and experimental structural parameters and CNO stretching frequencies. The (fulminato)metal complexes closely resemble the analogous cyano compounds.

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Liebig's Work on Metal Fulminates

Justus Liebig was born on May 12, 1803 in Darmstadt, Germany. His father owned a pigment and drug shop. Even as a boy he was fascinated by the crackers sold by the pedlars at the market,^[1–7] and he watched the preparation of this explosive. Liebig recognised that it was nitric acid

[‡] On the occasion of Liebig's 200th birthday.

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Wolfgang Beck, born in 1932, received his Ph.D. in 1960 at the Technische Hochschule (TH), München, under the supervision of Prof. W. Hieber. In 1968 he was appointed to the Chair of Inorganic and Analytical Chemistry at the Ludwig-Maximilians-Universität in München (LMU) and is now Emeritus Professor. His research interests are coordination and organometallic chemistry. He started his studies with metal complexes of pseudohalides (fulminato and azido ligands) and later proceeded to (among other topics) complexes of biologically important ligands. He has published over 600 papers and has been awarded the Liebig Medal of the Gesellschaft Deutscher Chemiker.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

which was used for the dissolution of silver or mercury with evolution of brown gases, and that the liquid which was added smelt of brandy and was alcohol. He probably repeated the preparation of silver fulminate in his father's small laboratory, where pigments were usually made and probably the metal fulminates were sold in his father's shop.^[5b] The synthesis of mercury and silver fulminate from ethanol, nitric acid, and mercury or silver was reported in 1800 by the English chemist Howard,^[8] and 107 years later the complicated process of fulminate formation was interpreted by Wieland in Munich.^[9] The young Liebig didn't like to study languages at the gymnasium in Darmstadt, so he left in 1817 aged 14 and started an apprenticeship in a pharmacy near Darmstadt where he stayed, although only for a few months. It is only a tale that Liebig caused an explosion (with metal fulminates?) in the school and in the pharmacy and therefore had to leave both.^[11,2] (However, the Liebig biography by Brock^[3] contains a painting of the explosion).

In these times — during the Napoleonic wars — there was a great demand for mercury fulminate. F. F. Runge has given an amusing report (F. Franz, *Grundriß der Chemie*, II. Teil, München, 1847) on his experience and accidents with mercury fulminate when he was a pharmacy apprentice in Lübeck in 1813.

Aged 17½, in 1820 Liebig was accepted by Karl Kastner — at that time one of the leading professors of chemistry — to study at the University of Bonn. Liebig (Figure 1) followed Kastner one year later to the University



Figure 1. Justus Liebig in 1821

5.

Einige Bemerkungen über die Bereitung und Zusammensetzung des Brugnatellischen und Howard'schen Knallsilbers.

(Vom Herrn Liebig, der Chemie Beflissenen aus Darmstadt *).

Es scheint vielleicht überflüssig, zu den vielen Vorschriften und Bereitungsarten dieses merkwürdigen Salzes noch eine neue hinzuzufügen; allein die älteren Angaben sind mehr oder weniger unbestimmt und unsicher, so, daß wenn man darnach arbeitet, ohne besondere Uebung das Präparat meistens mißlingt. Schon seit 2 Jahren verfertige ich nach der unten gegebenen Vorschrift eine

*) Die Leser mögen diese erste Probe des experimentellen Fleißes eines jungen Chemikers mit Nachsicht aufnehmen. Der Hr. Verf. widmete sich der Chemie bereits in Bonn mit achtungswerthem Eifer und setzte hier seine Studien in gleichem Geiste fort. Kastner.

Figure 2. Liebig's first publication

of Erlangen. In 1822 Liebig published his first paper^[10] on the safe preparation and some properties of silver fulminate (Figure 2). This paper contains also some chemical observations on silver fulminate by Kastner, and a kind remark on the skill and dedication of Liebig. In a subsequent, very short paper,^[11] Liebig reported that silver fulminate is soluble in aqueous ammonia solution and that NH_3 is formed on reaction with KOH .

In 1822 Liebig got into trouble with the citizens and the police as a member of a student unit, and he left Erlangen. With the aid of Kastner he was awarded a stipend by the Duke of Hessen, Ludwig I, for the study of chemistry at the Sorbonne in Paris, at that time the centre of the scientific study of chemistry, which was founded by Lavoisier. In Paris he could listen to the lectures of famous scientists such as Gay-Lussac, Thenard, Dulong, and Biot.^[1-3,5] In the small laboratory of Gaultier de Claubry (who discovered the reaction of iodine with starch) and with the support of Thenard, Liebig could continue his experiments with silver and mercury fulminate. Gay-Lussac presented Liebig's results before the Academy of Science in Paris, which attracted great attention. He himself demonstrated his new compounds at the meeting of the academy. In the publications on these results^[12,13] some very interesting remarks on fulminates are to be found: "It is now clear, that the detonating principle is due to a special acid." Liebig recognised the analogy between metal cyanides and metal fulminates, perhaps somewhat instinctively and said: "Although we find in detonating acids (fulminic acid) and det-

onating salts (metal fulminates) all the elements of cyanic acid they are not cyanides.”

Liebig^[13] reported the reactions of silver fulminate and of mercury fulminate with CaO, MgO, KOH, and NaOH. With copper, zinc, and iron he obtained explosive compounds which he called, for example, “real fulminating copper” (“wahres Knallkupfer”) and stated that the salts of fulminic acid (metal fulminates) belong to the most beautiful compounds in chemistry. He correctly formulated the products from the reaction of silver fulminate with, for example, CaO or KOH as double salts {in today’s terminology (fulminato)metal complexes like $K[Ag(CNO)_2]$ } and compared these compounds with (in our words) complexes of cyanide or of tartaric acid. Also the first experiments to analyze silver fulminate were carried out by Liebig,^[12,13] for instance, using 100 g (!) of silver fulminate and 400 g of magnesia (MgO) in a retort. Liebig found that the organic parts of silver fulminate and mercury fulminate have the same composition.^[12]

With AgCNO and aqueous ammonia Liebig obtained white crystals which proved to be so explosive and dangerous that they could not be handled. He reported several “terrible” explosions.^[13] Later several binary metal fulminates were obtained from $Hg(CNO)_2$ and amalgams of Na, K, Mn, Cu, Tl, and Cd.^[14]

Liebig was very courageous in his studies with the highly explosive and sensitive silver fulminate and used rather large quantities. In later days he admitted that any study with fulminates usually ended with an explosion, and further work was only started when the accident was gradually thrust into the background.^[2,15] In November 1830 — after a big explosion with solid silver fulminate and ammonium sulfide solution — Liebig wrote to Wöhler that he didn’t want to handle “fulminic acid” any more [“Liebig’s and Wöhler’s Briefwechsel in den Jahren 1829–1873” (Eds.: A. W. Hoffmann, E. Wöhler), Braunschweig, 1888; November 18th, 1830]. But Liebig obviously was a most skilful chemist and no serious injury was reported.

Liebig found that Berliner Blau (“Berlin Blue”) is formed from silver fulminate, KOH, and iron sulfate.^[13] Later this was confirmed by Schischkoff.^[16] Together with F. Lux it was shown^[16] that hexa(fulminato)ferrate(II) $[Fe(CNO)_6]^{4-}$ {and also $[Fe(CN)_5CNO]^{4-}$ ^[16]} is quantitatively reduced (deoxygenated) by $Fe(OH)_2$ to $[Fe(CN)_6]^{4-}$.

At the session of the academy, where Liebig’s results were so successfully presented,^[13] Alexander von Humboldt was present. Gay-Lussac and von Humboldt were close friends and they worked together on the law of combining gases (Gay-Lussac law).

Humboldt was highly impressed by the talent of Liebig and upon his recommendation Liebig was accepted in the laboratory of Gay-Lussac (Figure 3), where he could profit from Gay-Lussac’s and Thenard’s vast experience in the elemental analysis of organic compounds (Figure 4). In a short time the collaboration of Liebig and Gay-Lussac led to the perfect analysis of silver fulminate,^[17] a masterpiece of exact chemical work. Silver fulminate (200 mg) and copper oxide (8 g) were mixed and heated and gave CO_2 and



Figure 3. Joseph Louis Gay-Lussac (1778–1850)

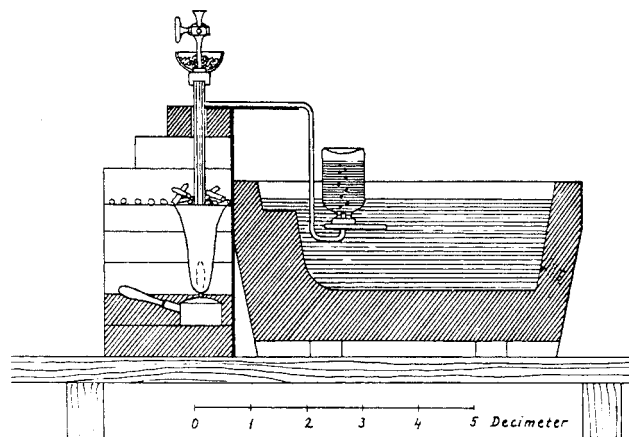


Figure 4. Gay-Lussac and Thenard’s apparatus for the combustion and analysis of organic substances (1810)

N_2 in the exact volume ratio 2:1 according to the equation $2 AgCNO + 2 CuO \rightarrow 2 Ag + 2 Cu + 2 CO_2 + N_2$

Previously, Gay-Lussac had analyzed hydrocyanic acid (HCN) by combustion with CuO to give CO_2/N_2 in the volume ratio 2:1 (Gay-Lussac, *Ann. Chim.* **1815**, *XCV*, 136–251).

In another quantitative experiment Liebig and Gay-Lussac determined the Ag content of silver fulminate after decomposition with hydrochloric acid, according to the equation



mass of AgCNO used: 2.266 g

mass of AgCl produced: 2.171 g (theoretical value 2.167 g)

They also correctly analyzed the reaction of silver fulminate with KCl according to the equation



mass of AgCNO used: 2.552 g

mass of AgCl found: 1.202 g (theoretical value 1.220 g)

In the latter case, the silver complex $[Ag(CNO)_2]^-$ is formed (which was called by Liebig “knallsaures Kali”).

Only half of the silver present in AgCNO was found in AgCl. The $K[Ag(CNO)_2]$ (“knallsaures Kali”) gave 1.210 g of AgCl after decomposition with HCl (compared with the theoretical value of 1.220 g). Thus, Liebig had discovered the first (fulminato)metal complex. Interestingly, $K[Ag(CNO)_2]$ is also formed by reaction with KBr in the solid state, as monitored by IR spectroscopy.^[18]

Next, Liebig and Gay-Lussac^[17] determined the carbon and nitrogen content of silver fulminate. A mixture of silver fulminate and copper oxide was carefully dried with CaCl_2 in a tube in vacuo using an air-pump. The measurements were carried out with the apparatus shown in Figure 5. The volumes of CO_2 and N_2 were measured with the apparatus developed by Gay-Lussac and Thenard (Figure 4).

It was found by five analyses (using 30 g of AgCNO for each analysis) from the volumes of CO_2 (which then was absorbed with KOH) and N_2 that 100 mg of AgCNO gave 17.16 mg (theory 17.35 mg) of cyanogen (CN). These analyses of AgCNO were really excellent: Ag: found 72.187, calcd. 71.97, CN: found 17.160, calcd. 17.35, O: found 10.653, calcd. 10.67.

Liebig and Gay-Lussac had carefully eliminated the possibility that silver fulminate contained hydrogen — this was confirmed by decomposition of a mixture of silver fulminate and K_2SO_4 .

Twenty years later Berzelius^[19] again questioned whether silver fulminate could contain hydrogen; this was immediately rejected by Liebig,^[19] as other arguments against his formulation were refuted with irony.^[20]

Liebig and Gay-Lussac^[17] also measured the gases which are formed from silver fulminate on detonation; they diluted AgCNO with KCl or K_2SO_4 and correctly concluded

that the residue must contain a “cyan” compound of silver (AgNCO !).

Finally, Liebig and Gay-Lussac^[17] came to the conclusion “that the various salts of fulminic acid contain the same acid which comprises one atom of cyanogen (CN) and one atom of oxygen”. In other words they had found the correct formulation (AgCNO). It is quite surprising and somewhat strange that it took about 70–80 years before Nef^[24] formulated fulminic acid as the monomeric oxime of carbon monoxide $\text{C}=\text{N}-\text{OH}$, and Lothar Wöhler proved the monomeric nature of the fulminate ion $\text{C}\equiv\text{N}-\text{O}^-$.^[25]

It was as late as 1965 that, together with K. Feldl,^[26] the structure of fulminic acid as formonitrile oxide $\text{H}-\text{C}\equiv\text{N}-\text{O}$ could be proven by its IR spectrum and that Winnenwiser et al.^[27,32] confirmed this structure by microwave spectroscopy and high resolution IR spectra. The HCNO structure could be deduced from the Huisgen^[31] 1,3-dipolar cycloaddition reactions of fulminic acid with unsaturated carbon compounds,^[22] which were performed by Quilico,^[28] and Huisgen and Christl.^[28] More recently, the mechanism of the cycloaddition reactions of HCNO was studied theoretically.^[29] L. Pauling^[30] calculated in 1926 from the mutual potential energy of the positive cores that fulminic acid has the formula HCNO rather than the tautomer CNOH , which was the possibility accepted at that time.

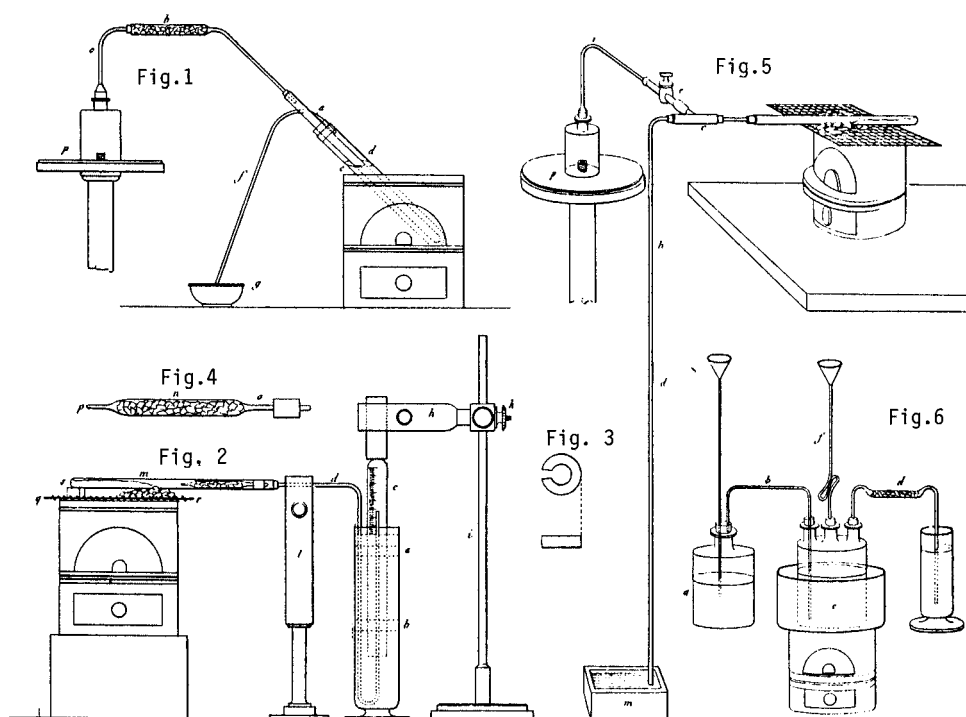


Figure 5. Apparatus used by Liebig and Gay-Lussac for the analysis of silver fulminate; legends in the figure itself (selection): Fig. 1: Drying of AgCNO with CaCl_2 and with an air-pump; Fig. 2: Determination of the volumes of CO_2 and N_2 after combustion of AgCNO with CuO using mercury; Fig. 4: Tube with CaCl_2 for the absorption of H_2O ; Fig. 5: Determination of the volumes of gases after thermal decomposition of an $\text{AgCNO}/\text{K}_2\text{SO}_4$ mixture; Fig. 6: Experiments to measure HCN from AgCNO and HCl (HCN was not observed); a) AgNO_3 for forming AgCN from HCN ; d) formation of H_2 from Zn and H_2SO_4 (in order to float HCN from the tube c); f) HCl

For excellent reviews of the long and fascinating history of fulminic acid, see refs.^[8,21–23] Interestingly in Munich there is a tradition of fulminic acid chemistry: J. v. Liebig, H. Wieland (who first proved the existence of the free fulminic acid^[9]) and R. Huisgen (1,3-dipolar cycloaddition reactions of HCNO^[28,31]). Fulminic acid and its derivatives have been studied extensively by many chemists. A list of citations on fulminic acid (which was kindly forwarded to the present author by M. Winnewisser) contains 140 titles from 1800 to 1966. After 1966 (ca. 180 papers were published up until 2003), fulminic acid attracted great attention from spectroscopists and theoreticians — mainly through the many important studies by M. and B. Winnewisser^[27,32] — because it proved to be a highly interesting unusual quasilinear molecule. The possible CHNO isomers and their stability attracted the interest of theoreticians.^[23,33]

HCNO can be prepared by several methods:^[22] a) By treatment of aqueous NaCNO solutions with sulfuric acid.^[9,26,27] b) From iodoformhydroxime [I(H)C=NOH] and base (NEt₃).^[28] This is obviously a method for preparative work; I(H)C=NOH has been obtained from NaCNO solutions and HI^[34] or more conveniently by Huisgen and Christl (avoiding the highly explosive NaCNO), directly from Hg(CNO)₂ and HI.^[28] c) By gas-phase pyrolysis of 3-phenyl-4-oxoiminoisoxazol-5(4H)-one^[35] (high yield) for spectroscopic measurements of HCNO.^[27] d) In situ preparation of HCNO by hydrolysis of trimethylsilylnitrile oxide Me₃SiCNO,^[36] which is accessible from Hg(CNO)₂ and Me₃SiBr.^[37] A reinvestigation of cycloaddition and polymerisation reactions of HCNO using this method has been reported.^[37]

In 1824, Friedrich Wöhler reported the synthesis of silver cyanate,^[38] which showed an identical analysis to silver fulminate. This proved to be one of the first examples of isomerism, a term which was coined after some discussion by Berzelius.^[39] However, at first Liebig^[40] did not believe these results (and at first Berzelius did not believe the silver fulminate analysis).

For a detailed discussion of the history of isomerism see: J. R. Partington, *A History of Chemistry*, Macmillan, London, 1964, vol. 4, p. 256; C. Graebe, *Geschichte der Organischen Chemie*, Springer, Berlin, 1920, p. 49.

Liebig^[40] repeated Wöhler's work and found a smaller content of oxygen in his silver cyanate sample which he called "cyanichte Säure". But Liebig had probably analyzed an impure sample of silver cyanate (containing AgCN), and later he confirmed Wöhler's findings, together with another analysis of silver fulminate.^[41] As it is well known,^[1–7] this was the beginning of a close and long-lasting friendship between Liebig and Wöhler. It may be mentioned that the present author has verified the fulminate (C≡N–O[–]) to cyanate (N=C=O[–]) isomerisation,^[42] for which a cyclic intermediate seems plausible.^[43]

To summarise, these experiments of Liebig were most important, mainly for three reasons:

- Through his studies of silver fulminate, Liebig was introduced to the field of elemental analysis, which, in 1830,

he developed into a general method in organic chemistry, by means of his ingenious five-sphere apparatus (Kali-Apparat; Figure 6).

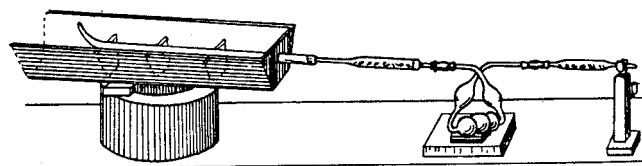


Figure 6. Liebig's method for elemental analysis for the absorption of H₂O (CaCl₂) and of CO₂ (KOH) with the five-spheres apparatus

- The identical analyses (but completely different properties) of silver fulminate (Liebig) and silver cyanate (Wöhler) led to the concept of isomerism.

- The work with metal fulminates decided Liebig's future scientific career, and won him — upon recommendation by Humboldt — a professorship at the University of Gießen at a very young age.

In the publication with Gay-Lussac,^[17] Liebig also reported reactions of silver fulminate with hydrochloric acid, hydroiodic acid, and hydrogen sulfide. The reaction of AgCNO with H₂S was later separately described by Liebig.^[45] This reaction was clarified later.^[45]

Liebig had wondered why no gas (HCN) was observed on reaction with hydrochloric acid (Figure 5). It was later found to be due to the formation of Cl(H)C=NOH.^[9,21,22,24]

In 1838, Liebig defined acids as compounds in which hydrogen can be replaced by metals (e.g. silver).^[46] Following this important definition, fulminic acid was considered by Liebig^[47] as a compound in which hydrogen can be substituted by a metal and in which hydrogen is bound to an oxygen-containing "radical".

Liebig published his last paper on metal fulminates in 1855^[48] and reported the oligomerisation of fulminic acid (by heating mercury fulminate in a diluted aqueous solution of KCl) to fulminuric acid; this was later studied by Wieland^[9,21] and Grundmann.^[22,49] Interestingly, Liebig gave, in his first and last publications on metal fulminates, a detailed and safe description for the preparation of silver^[10] and mercury^[48] fulminate. The preparation of the latter compound was later optimised,^[48] and mercury fulminate was also studied by Liebig's student August Kekulé in his habilitation thesis.^[50]

Further Developments

Structure of Silver Fulminate and Silver Cyanate

The interesting structure of silver fulminate, Liebig's favourite compound in his young years, was determined by Britton and Dunitz^[51] by X-ray crystallography. These X-ray structure determinations were later repeated and confirmed.^[51] It was found that AgCNO crystallises in two

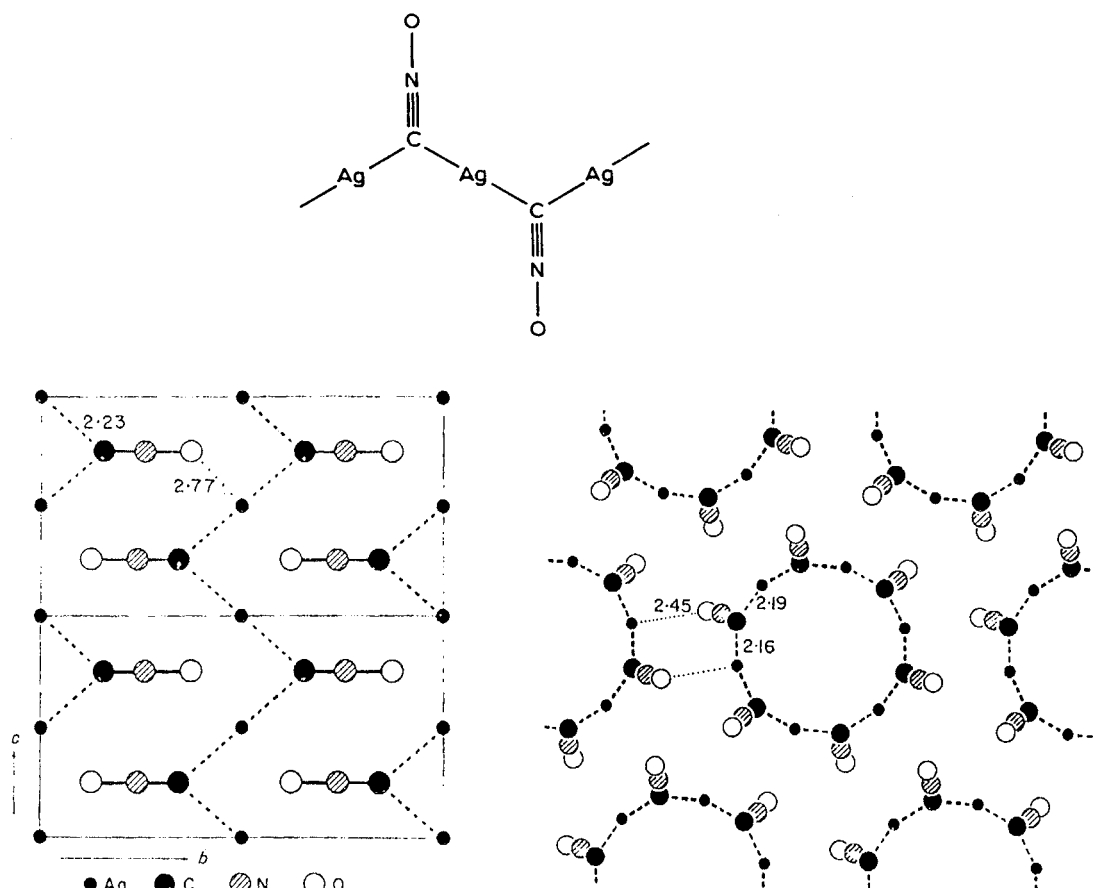


Figure 7. Structural element of orthorhombic (left) and trigonal (right) AgCNO in the crystal

polymorphic forms. In the orthorhombic form, infinite chains with fulminate bridges and three-centred Ag–C–Ag bonds are present (Figure 7), whereas the trigonal silver fulminate structure contains cyclic hexameric units, again with Ag–C–Ag bonds. The crystal structure of the isomeric silver cyanate AgNCO was also determined by Britton and Dunitz^[52] and shows Ag–N–Ag–N chains with NCO bridges, where each silver ion has two linearly coordinated N atoms. To the best of our knowledge a full crystal structure determination of mercury fulminate Hg(CNO)₂ has not been carried out.^[53] Mercury fulminate was widely used as explosive and was introduced by A. Nobel in 1867 as primary explosive to detonate dynamite.^[8,54] For this purpose it is now replaced in most industrial countries by lead azide, which is more stable to storage; mercury fulminate can react with metals in moist atmosphere.^[55]

Decomposition of Metal Fulminates

Liebig^[41] mentioned that oxides of metals (Ag, Hg) which readily lose oxygen form explosive salts of fulminic acid ("Oxide, welche ihren Sauerstoff leicht fahren lassen").

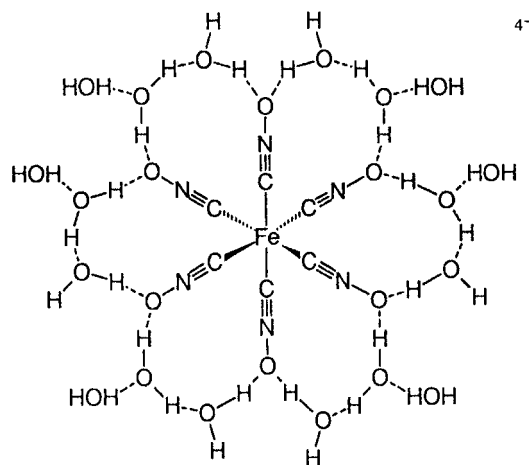
The thermal and photochemical decomposition of Hg(CNO)₂, AgCNO, and NaCNO was studied by Boddington and Iqbal.^[56] Gaseous metal, metal cyanate,^[42] CO₂, CO, N₂, and a polymeric material were identified as products by IR and mass spectra.^[56] Of interest is the ex-

remely high sensitivity of the ionic fulminates NaCNO or KCNO (in contrast to sodium azide, for example). It was suggested^[56] that electron transfer from the fulminate anion to sodium may be involved, to give CNO radicals. Recently, CNO radicals have been generated from anionic precursors in the gas phase.^[57] The dimer cyanogen di-*N*-oxide with the linear structure O–N≡C–C≡N–O was also generated in the gas phase.^[58] This compound was isolated by Grundmann^[22] from dichloroglyoxime and has a rich chemistry.^[22,58]

(Fulminato)metal Complexes

Formation of (Fulminato)metal Complexes

As mentioned, the first metal complex with fulminato ligands, K[Ag(CNO)₂], was obtained by Liebig^[12,13,17] from the reaction of silver fulminate with potassium chloride. This silver complex was later studied by Wieland.^[59] The hexa(fulminato)iron complex Na₄[Fe(CNO)₆]·18H₂O, the analogue of the cyanide [Fe(CN)₆]^{4–}, was discovered by Nef.^[24] It crystallises with 18 molecules of water, and one can speculate that its structure contains hydrogen bonds between the fulminato ligands and the water molecules (Figure 8).

Figure 8. Possible hydrogen bonding in $\text{Na}_4[\text{Fe}(\text{CNO})_6] \cdot 18 \text{H}_2\text{O}$

We found by IR spectroscopy that several (fulminato)-metal complexes like $[\text{Ni}(\text{phen})_3][\text{Ru}(\text{CNO})_6] \cdot \text{H}_2\text{O}$, $\text{Na}_4[\text{Fe}(\text{CNO})_6] \cdot 18\text{H}_2\text{O}$, and $\text{Na}_4[\text{Fe}(\text{CN})_5\text{CNO}] \cdot \text{H}_2\text{O}$ are only stable when water of crystallisation is present. On drying, the complexes decompose, with the formation of cyanate.^[18,60] Wieland described the explosive mercury complex $\text{Na}_2[\text{Hg}(\text{CNO})_4]$.^[61] The foundations for the coordination chemistry of the fulminate ion were laid by Lothar Wöhler in Darmstadt who, between 1914 and 1929, reported (with his coworkers Martin, Weber, and Berthmann) a series of homoleptic anionic (fulminato)metal complexes, isolated as highly explosive alkali or alkaline earth metal salts.^[62] Since that time (about 1930) fulminate complexes did not attract a great deal of attention. The present author studied these complexes in his habilitation work,^[18] because a metal–carbon bond had to be assumed, as in transition-metal complexes involving carbon monoxide, isocyanide, cyanide, and acetylide ligands. The coordination chemistry of the metal fulminates up until 1970 has been summarised.^[63,64] Therefore, in the following discussion, only the most important features and the newer results will be described. In our group,^[60,63] we found that fulminate complexes of transition metals can be stabilised by “diluting” the energy-rich metal–fulminate groups with large cations (AsPh_4^+ , PPh_4^+ , NR_4^+) or with large neutral ligands (e.g. PPh_3). This strategy was also very successfully applied to the isolation and characterisation of (azido)metal complexes, for example $[\text{AsPh}_4]_2[\text{Pt}(\text{N}_3)_6]$.^[65]

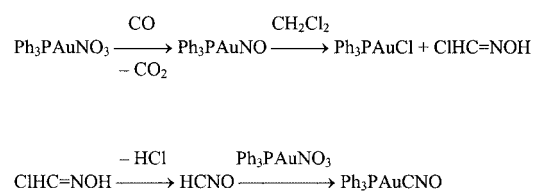
Usually, these (fulminato)metal complexes were prepared from aqueous sodium fulminate solutions and transition-metal salts, followed by the addition of tetraphenylarsonium chloride.^[60,63] The aqueous solution of NaCNO can be prepared from $\text{Hg}(\text{CNO})_2$ and sodium amalgam

under water.^[14,25,62,63] The known homoleptic anionic (fulminato)metal complexes are shown in Table 1; all correspond in their composition to cyano complexes, as it was first pointed out by Liebig^[12,13,17] (Table 1). The (fulminato)platinum complex *trans*- $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ could be obtained by oxidative addition of nitromethane to $[\text{Pt}(\text{PPh}_3)_4]$ in benzene/ethanol/water.^[66] Similarly, Ercolani et al.^[67] found that C–C cleavage of α -nitro ketones by platinum(II) and -(0) gives (fulminato)- and (carboxylato)-platinum(II) complexes. Presumably, the formation of fulminate occurs here via a (hydrido)(nitromethyl) complex. The isolation of σ -bonded nitromethyl complexes $[\text{R}(\text{R}_3\text{P})_2\text{PtCH}_2\text{NO}_2]$ from zerovalent platinum complexes and nitromethane^[68] and the observed conversion of $[\text{R}(\text{dppe})\text{PtCH}_2\text{NO}_2]$ to $[\text{R}(\text{dppe})\text{PtCNO}]$ by Bennett and co-workers^[69] support this assumption. Examples of other nitromethanide compounds are $[\text{R}_3\text{SnON}(\text{O})\text{CR}_2]$ ^[70] and $[(\text{terpy})\text{PtCH}_2\text{NO}_2]^+$.^[71]

Nef^[24] and Wöhler^[25] showed that mercury fulminate is formed from the sodium salt of nitromethane and HgCl_2 . In addition, organomercury fulminate compounds RHgCNO can be prepared from RHgOH and CH_3NO_2 .^[72] Organomercury fulminates RHgCNO are easily formed by synproportionation of diorganylmercury and mercury fulminate^{[73][74]} and can undergo Huisgen^[31] [2 + 3] cycloaddition reactions.^[74]

$[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ {which is also accessible from $[\text{Pt}(\text{CNO})_4]^{2-}$ and PPh_3 ^{[75]}} is best prepared by reaction of $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)]$ with nitromethane,^[76] since with $[\text{Pt}(\text{PPh}_3)_4]$ an excess of PPh_3 can lead to reduction of fulminate to give the (cyano)metal complex $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CN})_2]$.

A very interesting source of the fulminato ligand is CH_2Cl_2 , CO, and nitrate. Bos, Steggerda et al.^[77] discovered the formation of the (fulminato)metal complex $[\text{Ph}_3\text{PAuCNO}]$ and the cluster compound $[\text{Au}_{11}(\text{PPh}_3)_8(\text{CNO})_2]^+\text{NO}_3^-$ by reaction of $[\text{Ph}_3\text{PAuNO}_3]$ or of $[\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)]$ with carbon monoxide in dichloromethane. It was suggested that the fulminate ligand is formed by reduction of $[\text{Ph}_3\text{PAuNO}_3]$ with CO to $[\text{Ph}_3\text{PAuNO}]$, which reacts with CH_2Cl_2 to afford chloroformoxime (Scheme 1). It was demonstrated by ^{13}C O



Scheme 1

Table 1. Homoleptic anionic (fulminato)metal complexes

$[\text{Fe}(\text{CNO})_6]^{4-}$	$[\text{Co}(\text{CNO})_6]^{3-}$	$[\text{Ni}(\text{CNO})_4]^{2-}$	$[\text{Cu}(\text{CNO})_2]^-$	$[\text{Zn}(\text{CNO})_4]^{2-}$
$[\text{Ru}(\text{CNO})_6]^{4-}$	$[\text{Rh}(\text{CNO})_6]^{3-}$	$[\text{Pd}(\text{CNO})_4]^{2-}$	$[\text{Cu}(\text{CNO})_3]^{2-}$	$[\text{Cd}(\text{CNO})_4]^{2-}$
—	$[\text{Ir}(\text{CNO})_6]^{3-}$	$[\text{Pt}(\text{CNO})_4]^{2-}$	$[\text{Ag}(\text{CNO})_2]^-$	$[\text{Hg}(\text{CNO})_4]^{2-}$
			$[\text{Au}(\text{CNO})_2]^-$	

experiments that the carbon atom of CNO^- originates from CH_2Cl_2 .^[77] Dehydrochlorination of chloroformoxime with base gives fulminic acid, which can form the (fulminato)-metal complexes. Already Nef^[21,22,24] had reported the formation of AgCNO from chloroformoxime and a silver salt.

An unexpected metal cluster with a fulminate bridge $[(\text{C}_5\text{Me}_5)_3\text{Mo}_3(\text{CO})_4(\mu_3\text{-O})(\mu_2\text{-CNO})]$ was reported by Dahl et al.^[78] from the photochemical reaction of $[(\text{C}_5\text{Me}_5)_3\text{Mo}_3(\text{CO})_4(\text{O})(\text{N})]$ with CO .

Some (fulminato)metal complexes with the metal atom in a low oxidation state could be obtained from the reaction of the hexacarbonyl compounds of Cr, Mo, and W with sodium fulminate^[60] as well as from the reaction of $\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{Br}]$ with AgCNO (**Caution!**),^[79] for example $[\text{M}(\text{CO})_5\text{CNO}]^-$ and $[\text{M}(\text{CO})_4(\text{CNO})_2]^{2-}$ (as AsPh_4^+ or NEt_4^+ salts; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$).

Reactivity of (Fulminato)metal Complexes

Reduction $\text{M}-\text{C}\equiv\text{N}-\text{O} \rightarrow \text{M}-\text{C}\equiv\text{N}$

The fulminate ligand can be reduced to the cyano group; for example, $[\text{Fe}(\text{CNO})_6]^{4-}$ and $[\text{Fe}(\text{CN})_5(\text{CNO})]^{4-}$ can be deoxygenated with $\text{Fe}(\text{OH})_2$ to give $[\text{Fe}(\text{CN})_6]^{4-}$.^[16] Like nitrile oxides,^[22] the metal-coordinated fulminate ion can also be deoxygenated with phosphanes; for example, the (cyano)metal complex *trans*- $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CN})_2]$ is formed from the reaction of *trans*- $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ with PR_3 ($\text{R} = \text{Ph}, \text{OEt}$). The intermediate $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})(\text{CN})]$ could be detected by its IR spectrum.^[80] The deoxygenation of the fulminato ligand at the metal atom is chemical proof that the fulminate ion is bonded to the metal atom through the carbon atom.^[16,18,64a]

Isomerisation $\text{M}-\text{C}\equiv\text{N}-\text{O} \rightarrow \text{M}-\text{N}=\text{C}=\text{O}$

Thermal isomerisation of fulminate (at temperatures above 200 °C) to the much more stable^[81] isocyanate has been observed for several complexes.^[60,63,67,79] As for the fulminate anion^[42,43] and nitrile oxides,^[22,82] the rearrangement may occur via a cyclic intermediate.

The isomerisation of CNO to NCO was also observed during attempts to stabilise the isofulminic acid or fulminic acid ether complexes ($\text{M}-\text{C}\equiv\text{N}-\text{OH}$ or $\text{M}-\text{C}\equiv\text{N}-\text{OR}$) by reaction of $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ with acetic acid or Et_3OBF_4 ,^{[79][80]} in a similar manner to the formation of hydrogen isocyanide by protonation of cyano complexes.^[83] Until now isofulminic acid (HONC) could not be detected, even not by the elegant and thorough studies of Maier and co-workers.^[84] However, Wentrup and co-workers^[85] were able to generate “organic fulminates” $\text{R}-\text{O}-\text{N}\equiv\text{C}$ from 4-oximinoisoxazol-5(4*H*)-ones.

The isomerisation of $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ to $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{NCO})_2]$ occurs in the presence of organic carbonyl compounds (e.g. acetone, benzaldehyde) at much lower temperatures.^[80] This can be explained by a Huisgen [2+3] cycloaddition of the carbonyl group to the fulminato ligand, to give an (unstable) dioxazolone, similar to nitrile oxides.^[22,31,86] The formation of $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{NCS})_2]$ ^[80] from $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ and CS_2 or thiobenzophenone can be

attributed to a [2+3] cycloaddition of the C–S group to the fulminato ligand — as occurs with organic nitrile oxides^[22] — and subsequent elimination of COS or benzophenone, respectively.

Substitution of the fulminato ligand in $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ by Ph_4AsCN led to Ph_4AsCNO , from which several (fulminato)metal complexes could be safely prepared.^[80]

Reactions of Nitrile Oxides with Metal Complexes

The reactions of nitrile oxides with $\text{Co}_2(\text{CO})_8$ resulted in deoxygenation to the corresponding nitriles.^[87] By reaction of stable nitrile oxides with zerovalent platinum complexes $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{L})]$ ($\text{L} = 2 \times \text{PPh}_3, \text{C}_2\text{H}_4$) the nitrile oxide is deoxygenated and one of the phenyl groups on PPh_3 migrates to the platinum atom to give the complexes $[(\text{Ph}_3\text{P})(\text{RCN})\text{Pt}(\text{OPPh}_2)(\text{Ph})]$,^[88] in which the OPPh_2 group is bonded by the P atom to the metal atom. The only complex in which an intact RCNO group is present appears to be the cluster $[\text{Cp}_3\text{Co}_3(\mu_3\text{-CR})(\mu_2\text{-RCNO})]$ which is formed from $\text{Cp}_3\text{Co}_3(\mu_3\text{-CR})_2$ and NO^+ .^[89]

With electron-rich carbonyliridium complexes, nitrile oxides undergo Huisgen [2+3] cycloadditions (with the metal–carbon bond as the 1,3-dipolarophile) to give metallacycles $[\text{L}_n\text{M}-\text{C}^a(\text{R})=\text{N}-\text{O}-\text{C}^b(\text{O})(\text{M}-\text{C}^b)]$.^[90] Interestingly, decomposition of these metallacycles gives π -bonded nitrile complexes and can lead to activation of C–H bonds.^[90]

Spectra

The IR spectra of binary metal fulminates^[42,91] and of (fulminato)metal complexes^[18,63,64b,92] are particularly characteristic. The overtone of the $\nu_s(\text{CNO})$ [$\nu(\text{NO})$] stretching vibration (at ca. 1100 cm^{-1}) absorbs near the $\nu_{as}(\text{CNO})$ band. So, Fermi resonance occurs, and two strong bands appear in the region 2000–2200 cm^{-1} . This is typical for metal fulminates, which can thus be easily identified by their IR spectra. It was observed that $\nu_{as}(\text{CNO})$ and $\nu_s(\text{CNO})$ are coupled, that is, they move in the same direction for various metal fulminates.^[63] Also ^{15}N -containing metal fulminates^[93a] and (fulminato)metal complexes^[92] have been studied and the frequencies of coordinated cyanate and fulminate groups have been theoretically analyzed.^[64b,94] The metal isotope technique was employed to assign the iron–CNO stretching vibration at 533 cm^{-1} of $\text{Fe}(o\text{-phenanthroline})_2(\text{CNO})_2$.^[93b] DFT calculations of $\nu_{as}(\text{CNO})$ and $\nu_s(\text{CNO})$ frequencies of (fulminato)metal complexes are in very good agreement with the observed data.^[95]

The ^{14}N chemical shifts in the NMR spectra of metal fulminates are similar to those of nitrile oxides and differ considerably from those of isomeric isocyanate complexes.^[96]

The electronic spectra of fulminate complexes reveal that the fulminato ligand is near cyanide in the spectrochemical series^[97] (just a little lower in ligand field strength) and also has a similarly strong *trans* influence.^[98]

Table 2. Bond lengths [pm] and angles [°] in metal fulminates

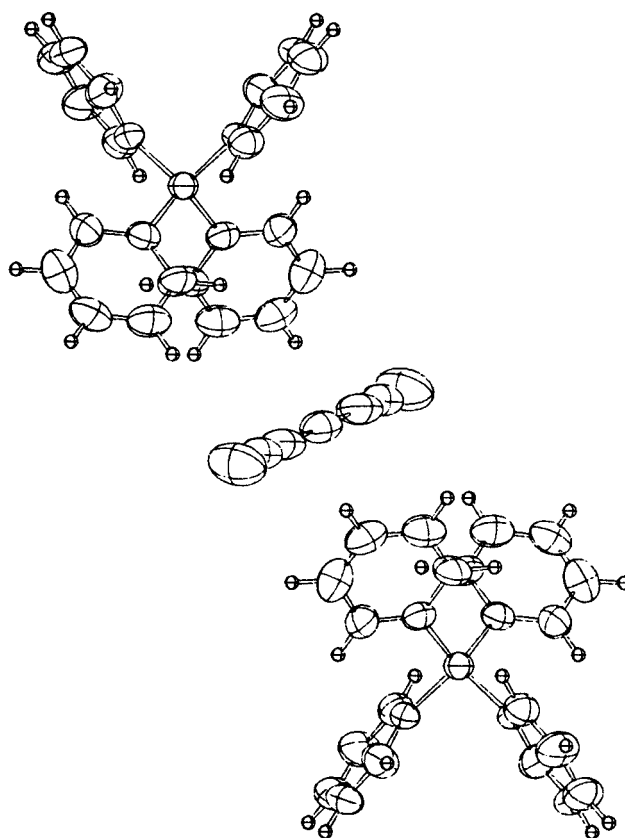
	Ref.	M–C	C≡N	N–O	M–C≡N	C≡N–O
(Ph ₃ P) ₂ Pt(CNO) ₂	[76]	198	113	127	179	178
[Au(CNO) ₂] [−]	[103]	201	110	125	179	178
[Ph ₃ PAuCNO]	[104]	194	115	127	163	179
AgCNO	[51]	218	116	125		180
[Hg(CNO) ₄] ^{2−}	[100]	219	114	125	173	179
[Co(CNO) ₆] ^{3−}	[101]	191	113	127	178	178
[Ni(CNO) ₄] ^{2−}	[102]	187	114	126	174	179
[Pt(CNO) ₄] ^{2−}	[102]	199	115	126	179	179
[Zn(CNO) ₄] ^{2−}	[102]	200	114	125	178	179

The formation constant of [Hg(CNO)₄]^{2−} has been determined ($K_2 = 10^{36}$). This is smaller than that for [Hg(CN)₄]^{2−} by a factor of 10^5 , but it is nevertheless still high.^[99]

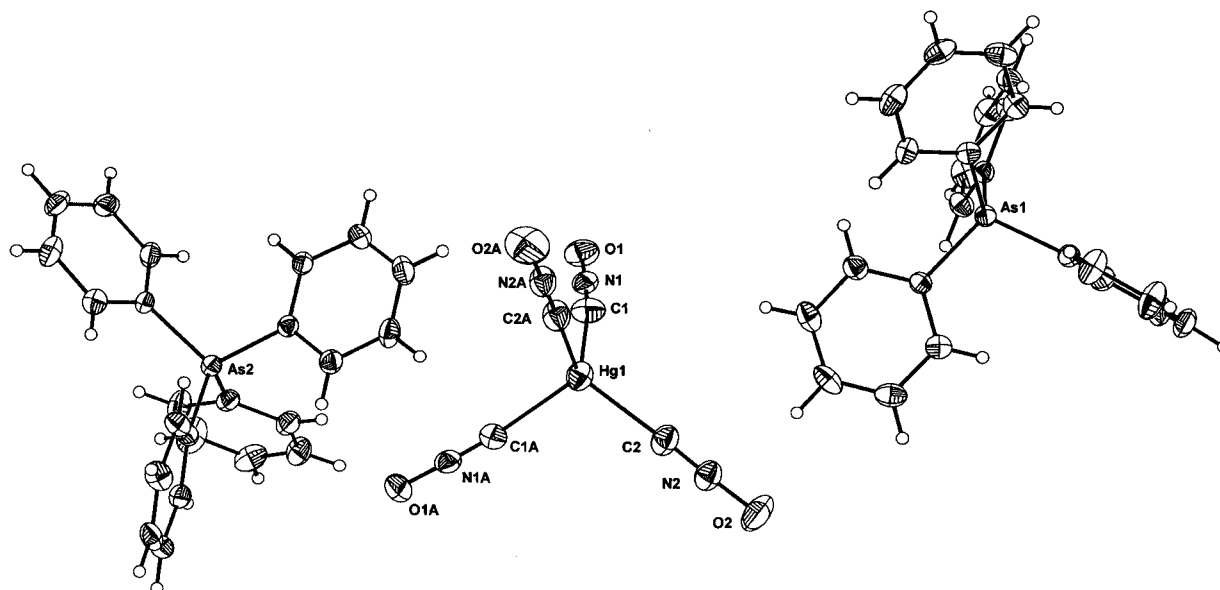
Crystal and Molecular Structures of (Fulminato)metal Complexes

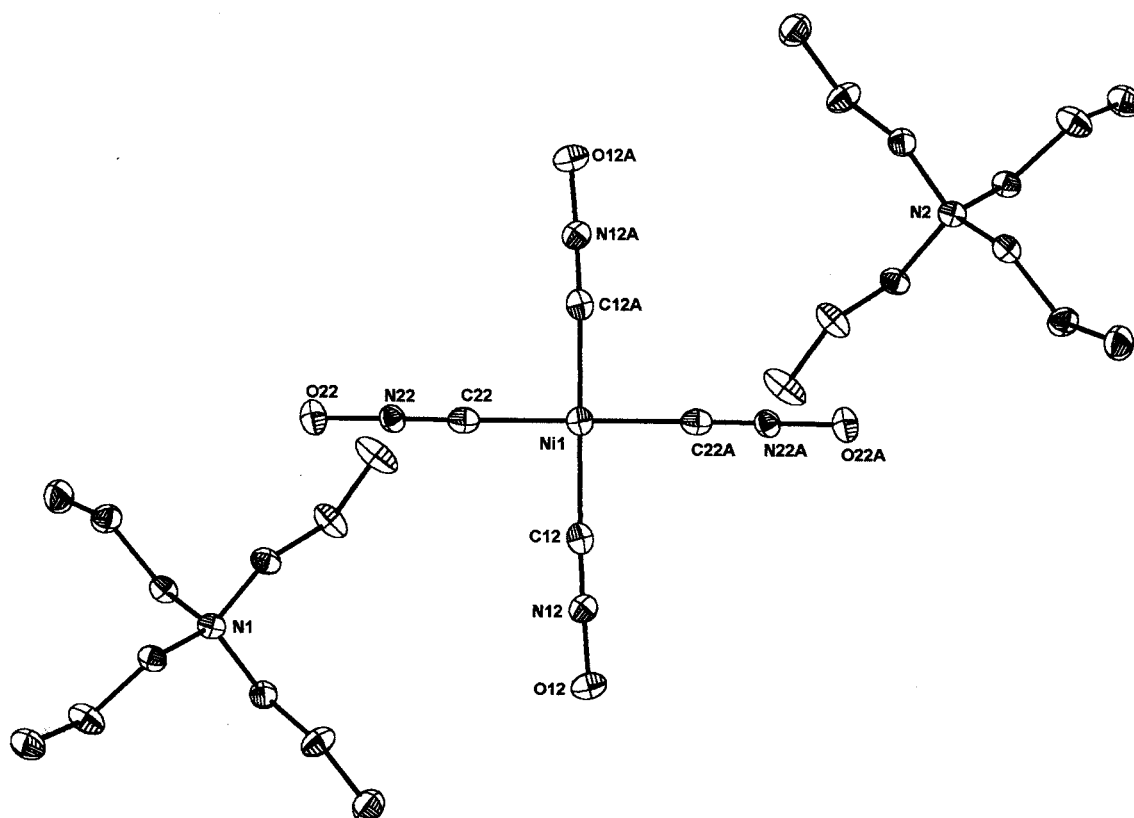
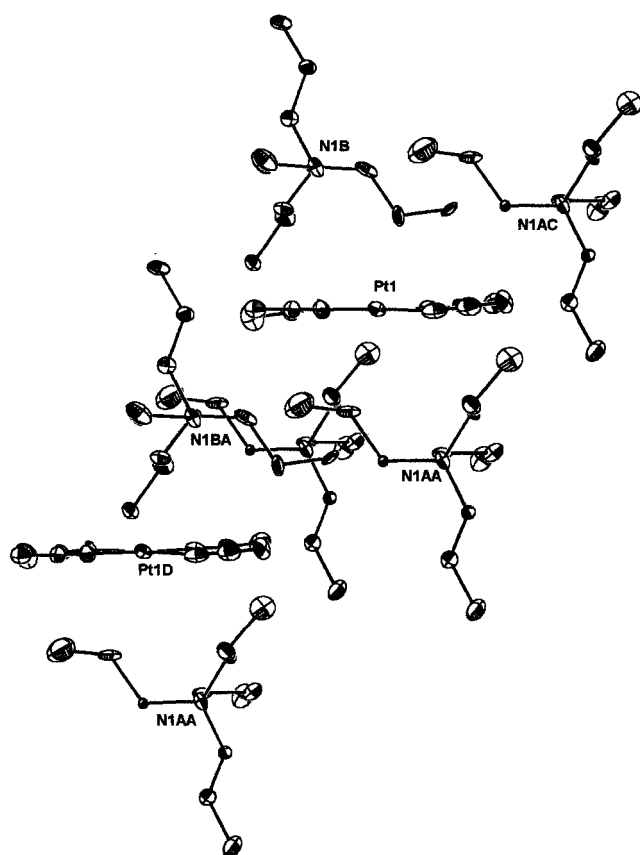
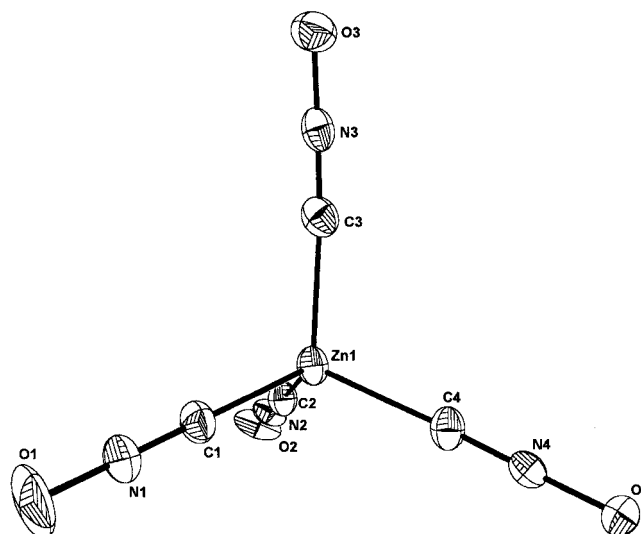
Recently, a series of (fulminato)metal complexes, which had been prepared about 35 years ago and which “survived”, were structurally characterised by X-ray diffraction.^[100–102]

Table 2 shows the (fulminato)metal complexes, which have so far been studied by X-ray diffraction. In the crystals of, for example, [AsPh₄][Au(CNO)₂], [AsPh₄]₂[Hg(CNO)₄], [N(C₃H₇)₄]₂[Ni(CNO)₄], and [N(C₃H₇)₄][Pt(CNO)₄], it is clearly evident that in the crystal the energy-rich (fulminato)metallate anions are separated and surrounded by the large cations (Figures 9–12). So the metal fulminate groups are “diluted” and the fulminate compounds are thermally stabilised. Already the IR and Raman spectra had indicated the high symmetry of the homoleptic anionic (fulminato)-metal complexes, since only one $\nu_{\text{as}}(\text{CNO})$ and $\nu_{\text{s}}(\text{CNO})$ absorption was observed in the solutions of these com-

Figure 9. Crystal structure of AsPh₄[Au(CNO)₂]

pounds.^[18,63,92] The X-ray structure determinations of the AsPh₄⁺ salts of [Au(CNO)₂][−],^[103] [Hg(CNO)₄]^{2−},^[100] [Ni(CNO)₄]^{2−},^[102] [Pt(CNO)₄]^{2−},^[102] [Zn(CNO)₄]^{2−},^[102] and [Co(CNO)₆]^{3−}^[101] reveal the almost ideal linear, tetrahedral, square-planar or octahedral structure of these anions (Figures 9–14).

Figure 10. Crystal structure of [AsPh₄]₂[Hg(CNO)₂]

Figure 11. Crystal structure of $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Ni}(\text{CNO})_4]$ Figure 12. Crystal structure of $[\text{N}(\text{C}_3\text{H}_7)_4]_2[\text{Pt}(\text{CNO})_4]$ Figure 13. Crystal structure of $[\text{Zn}(\text{CNO})_4]^{2-}$

The bonding parameters of the (fulminato)metal complexes are very similar (Table 2) with $\text{C}\equiv\text{N}$ and $\text{N}-\text{O}$ bond lengths of 114–116 pm and 125–126 pm, respectively, and $\text{M}-\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{N}-\text{O}$ angles close to 180° . Remarkably, the metal–C and $\text{C}\equiv\text{N}$ bond lengths in corresponding (fulminato)- and (cyano)metal complexes are almost identical (Table 3). Therefore, the formula $\text{M}-\text{C}\equiv\text{N}-\text{O}$ is a good description for the bonding in fulminato complexes. As mentioned earlier, Liebig emphasised the analogy be-

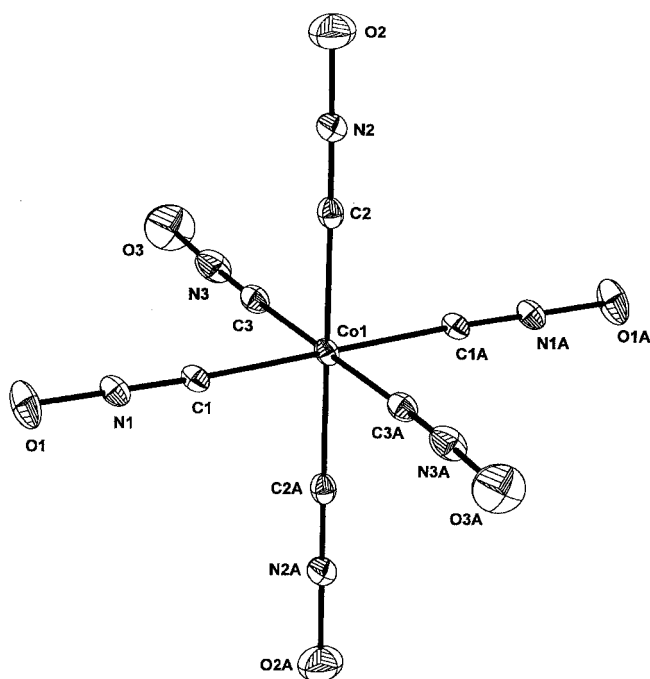
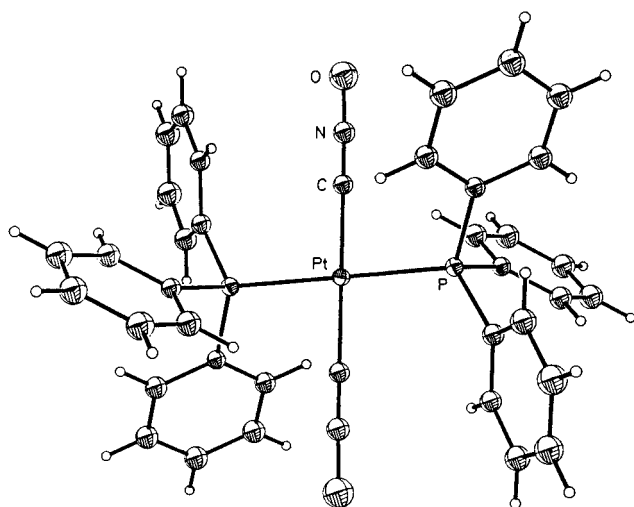
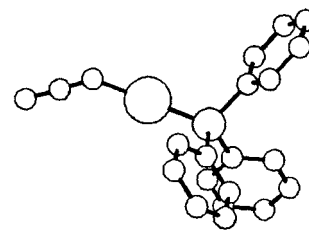
Figure 14. Crystal structure of $[\text{Co}(\text{CNO})_6]^{3-}$

Table 3. Bond lengths [pm] in (cyano)- and (fulminato)metal complexes

	Ref.	M–C	C≡N
$[\text{Hg}(\text{CNO})_4]^{2-}$	[100]	219	114
$[\text{Hg}(\text{CN})_4]^{2-}$	[105]	218	114
$[\text{Co}(\text{CNO})_6]^{3-}$	[101]	191	113
$[\text{Co}(\text{CN})_6]^{3-}$	[106]	189	115
$[\text{Ni}(\text{CNO})_4]^{2-}$	[102]	187	114
$[\text{Ni}(\text{CN})_4]^{2-}$	[107]	186	113
$[\text{Pt}(\text{CNO})_4]^{2-}$	[102]	199	115
$[\text{Pt}(\text{CN})_4]^{2-}$	[108]	ca.200	ca.115
$[\text{Zn}(\text{CNO})_4]^{2-}$	[102]	200	114
$[\text{Zn}(\text{CN})_4]^{2-}$	[109]	202	116

Figure 15. Crystal structure of $\text{trans}-[(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2]$ Figure 16. Crystal structure of $[\text{Ph}_3\text{PAuNCO}]$

tween metal cyanides and fulminates.^[12,13,17] The fulminate ion, which is best formulated as $\text{C}\equiv\text{N}-\text{O}^-$,^[42,91,93] behaves predominantly as a σ -donor to the metal ion through an sp-carbon atom in the linear $\text{M}-\text{C}\equiv\text{N}-\text{O}$ group (Figures 9–15), whereas the metal isocyanate group $\text{M}-\text{N}=\text{C}=\text{O}$ is bent with an sp^2 -nitrogen atom (e.g. in $\text{Ph}_3\text{PAu}-\text{N}=\text{C}=\text{O}$,^[104] Figure 16). DFT (Density Functional Theory) calculations by Klapötke^[95] are in good agreement with the observed structural parameters (Table 4).

Table 4. Observed (X-ray) and computed structural parameters

Complex anion	Sym.	$d(\text{M}-\text{C})$ [Å] calcd./exptl.	$d(\text{C}-\text{N})$ [Å] calcd./exptl.	$d(\text{N}-\text{O})$ [Å] calcd./exptl.
$[\text{Co}(\text{CNO})_6]^{3-}$	O_h	1.919/1.915(6)	1.181/1.130(6)	1.269/1.269(6)
$[\text{Ni}(\text{CNO})_4]^{2-}$	D_{4h}	1.863/1.875(5)	1.184/1.138(5)	1.259/1.261(4)
$[\text{Zn}(\text{CNO})_4]^{2-}$	T_d	2.044/2.005(4)	1.187/1.140(4)	1.253/1.250(4)
$[\text{Pt}(\text{CNO})_4]^{2-}$	D_{4h}	2.008/2.00(2)	1.184/1.16(3)	1.257/1.25(2)
$[\text{Au}(\text{CNO})_2]^-$	$D_{\infty h}$	1.985/2.01(2)	1.187/1.10(3)	1.241/1.25(2)
$[\text{Hg}(\text{CNO})_4]^{2-}$	T_d	2.248/2.218(8)	1.188/1.150(9)	1.252/1.256(8)

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