

Figure 2. I.r. spectra of CO-O₂ interaction at 77 K on a reduced Cu/ZnO sample: curve (a) CO on a preoxidized sample; curve (b), 5 Torr of O₂ on a sample previously covered with CO (the CO coverage corresponds to 5 min of outgassing).

and 2116 cm⁻¹ respectively. In curve (b) the band at 2198 cm⁻¹ has a lower intensity, the 2140 cm⁻¹ one does not appear, while the bands at 2116 and 1580 cm⁻¹ immediately appear, accompanied by minor absorptions at 1620, 1520, 1330, and 1290 cm⁻¹ assigned to carbonate-like species.⁷

The bands at 2140 and 2116 cm⁻¹ have previously been assigned to CO adsorbed on borderline oxidized Cu atoms and on oxidized Cu atoms of extended surface areas respectively.²

On the basis of the contemporaneous lack of the 2198 and 2140 cm⁻¹ bands when the 1580 cm⁻¹ one is present, we can infer that the 1580 cm⁻¹ related species is bonded to both a zinc ion and a Cu borderline site; the oxidation of the CO-precovered surface makes the formation of this species easier as a consequence of electron withdrawal from the surface, favouring the formation of the four-electron donor species.

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The Structures of Lithium and Magnesium Derivatives of Acetic Acid 'Dianions'

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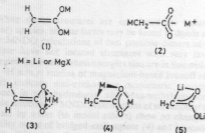
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Ab initio and semi-empirical MNDO calculations indicate that monomeric dilithiated and bis-magnesium derivatives of carboxylic acids (Ivanoff reagents) favour the 1,3-1,3' doubly bridged structures generally found in metallated Y-conjugated dianion systems.

Metallation of carboxylate salts possessing α -hydrogens by alkylmagnesium derivatives was first observed at the beginning of the century by Grignard.¹ The bifunctional metal derivatives resulting from this reaction were shown by Ivanoff and coworkers to be quite versatile synthetically.²⁻³ The highly stereospecific addition of Ivanoff reagents to carbonyl com-

pounds is usually attributed to an early cyclic transition state involving the bis-enolate of the reagent (1)³ and this form is usually considered to be the structure of the reagent itself.³ Dilithiated carboxylic acids are also widely employed synthetic reagents;⁴ these have been formulated as 'ate'⁵ or as C-metallated derivatives, e.g. (2). Studies of bifunctional



polar organometallic derivatives of carboxylic acids by physical methods such as i.r.⁶ and n.m.r. spectroscopy,⁷ indicate that there is only one isomer in solution, but have not established its nature. No X-ray structures are available yet.

We report a model theoretical study of dilithium and bis-magnesium (MgH) derivatives of acetic acid. Our earlier work on the Y-conjugated dianions^{8,9} has demonstrated the close correspondence between the results of such calculations and experimental structures.¹⁰

Ab initio MO calculations for $\text{C}_2\text{H}_2\text{Li}_2\text{O}_2$ and $\text{C}_2\text{H}_2\text{Mg}_2\text{O}_2$ isomers were carried out with the GAUSSIAN series of computer programs.¹¹ All geometries were completely optimized with the 3-21G basis set.¹² In addition, single point 6-31G¹³ and MP2/6-31G¹⁴ calculations were performed on the most stable forms of $\text{C}_2\text{H}_2\text{Li}_2\text{O}_2$, but no qualitative differences in the energy orderings were found. Semi-empirical MNDO theory¹⁵ was used to study the association of dilithioacetate ben-enolate and carboxylate forms and to model solvation by water, simulating ether solvents.

Several symmetrically 1,4- and 1,5-doubly bridged organolithium compounds are now known;^{9,10,16} this suggests (3) as a candidate for the most stable structure. However, 1,3-double bridging is less favourable energetically¹⁶ and lithiated Y-conjugated dianion systems are known to favour less symmetrical metal placements as in (4).^{8,9} Indeed, the 3-21G//3-21G results on $\text{C}_2\text{H}_2\text{Li}_2\text{O}_2$ indicate (4) (M = Li, -240.285 34 a.u.)[†] to be the most stable isomer and (3) (M = Li, -240.272 66 a.u.) to be the best alternative, 33.3 kJ mol⁻¹ higher in energy. The singly bridged (5) (-240.257 26 a.u.) and the classical (1) (M = Li, -240.249 24 a.u.) are not competitive; even less so at the higher theoretical levels. In the 3-21G structure of (4) (M = Li, Figure 1), one lithium is roughly in the carboxylate plane while the second is involved in π -enolate anion bridging.⁸ The electrostatic ion triplet interactions are more important than π -delocalization; the C_s form of (4) (M = Li), with both lithiums in the same plane and the CH_2 group twisted to 'shut off' the enolate resonance, is only 50 kJ mol⁻¹ higher in energy.

Calculations of structures similar to (1), (3), and (4) were also carried out for bis-magnesiumacetate, $\text{C}_2\text{H}_2\text{Mg}_2\text{O}_2$. Organomagnesium derivatives are less polar than their lithium counterparts, C-Mg bonds are more covalent, and magnesium has a lowered bridging tendency.¹⁷ However, in the present case magnesium does not show qualitative difference from lithium and the most stable form (4) is quite similar in geometry (M = MgH, Figure 2). The 3-21G//3-21G order of stability of bis-magnesium isomers (4) (M = MgH, -623.563 79 a.u.) > (3) (M = MgH, -623.543 41 a.u.) > (1) (M = MgH, -623.525 75 a.u.) is the same as that found for the corresponding dilithium derivatives. No minimum was found for a structure similar to (5).

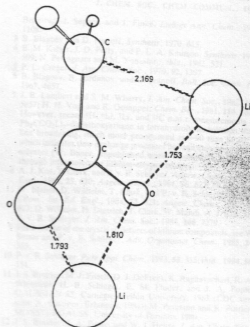


Figure 1. Calculated (3-21G basis set) structure of (4) (M = Li), the most stable form of dilithiated acetic acid.

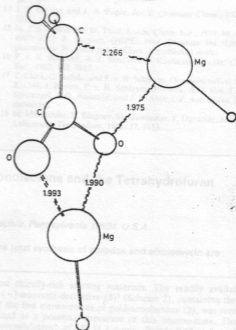


Figure 2. Calculated (3-21G basis set) structure of (4) (M = MgH), a model for the magnesium-based Ivanoff reagent. Note the similarity with Figure 1.

[†] 1 a.u. = 2625.46 kJ mol⁻¹.

While these structures are calculated for isolated (gas phase) species, similar forms may be found in donor solvents. Our MNDO calculations of two possible dimers of dithioacetate have not located structures with very favourable energies. Low association energies also are in line with the ^{13}C and ^1H n.m.r. studies of magnesium-based Ivanoff reagents, which indicate non-exchanging monomeric species to be present in tetrahydrofuran and hexamethylphosphor triamide solutions.¹⁸ MNDO calculations of solvation of dithioacetate by water (to model ethers) show no changes of the stability order of bridged carboxylate (4) and bis-enolate (1) forms. While the first solvation step of dithioacetate is favourable (an average of -16.0 kcal mol $^{-1}$ per complexation of a H_2O molecule with each lithium atom), further solvation of (4) is calculated to be endothermic. This is consistent with the experimentally known tendency of crystallosolates of Ivanoff reagents to lose solvent ligands.¹⁸ The bis-enolate form (1) is predicted to be better solvated than (4). While the average solvation energy for the first solvation of (1) is nearly the same (-16.2 kcal mol $^{-1}$), the energy of the second H_2O attachment also is favourable. Hence, solvation reduces the energy difference between (4) and (1), but the former is still more stable.

The present *ab initio* and MNDO calculations predict that monomeric Ivanoff reagents, dilithium and bis-magnesium derivatives of carboxylic acids, probably have the bridged structures exhibited by other metallated Y-dianions in the presence of ether solvents.*

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† 1 kcal = 4.184 kJ.

Carbohydrate-based Syntheses of the Goldinonolactone and the Tetrahydrofuran Fragments of Aurodox and Eftromycin

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Carbohydrate-based syntheses of two key intermediates for the total synthesis of aurodox and eftromycin are reported.

Aurodox (1) and eftromycin (2) (Scheme 1) are two of the most important members of the efamycin family of antibiotics.¹ We have recently reported the first total synthesis of these complex molecules in which fragments (3) (goldinonolactone) and (4) (Scheme 1) served as key intermediates.² Their construction was based on acyclic stereoselection techniques starting with prochiral compounds. In this communication, we describe alternative and efficient routes to these subtargets (3) and (4) based on a carbohydrate approach

and chirally-rich starting materials. The readily available L-(-)-mannose derivative (5)³ (Scheme 2), containing three of the five stereocentres of goldinonolactone (3), was recognized as a potential precursor of this intermediate. Thus, monosilylation† of (5) (1.1 equiv. $\text{Bu}(\text{Me}_2\text{SiCl})_2$, 1.3 equiv.

† All new compounds exhibited satisfactory spectroscopic and analytical data.

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